Homogeneous CO Hydrogenation: Ligand Effects on the Lewis Acid Assisted Reductive Coupling of Carbon Monoxide

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Supporting Information

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I. General Considerations.

All air- and moisture-sensitive compounds were manipulated using standard vacuum line or Schlenk techniques, or in a glovebox under a nitrogen atmosphere. Under standard glovebox conditions, petroleum ether, diethyl ether, benzene, toluene, and tetrahydrofuran were used without purging, such that traces of those solvents were in the atmosphere, and could be found intermixed in the solvent bottles. The solvents for air- and moisture-sensitive reactions were dried over sodium benzophenone ketyl, calcium hydride, or by the method of Grubbs.[1] All NMR solvents were purchased from Cambridge Isotopes Laboratories, Inc. Benzene-d_6 was distilled from sodium benzophenone ketyl or titanocene. Dichloromethane-d_2 and chlorobenzene-d_5 were distilled from calcium hydride and run through a small column of activated alumina. Tetrahydrofuran-d_8 was purchased in a sealed ampoule, and dried by passage through activated alumina. Unless noted, other materials were used as received. $Re(CO)_5Br$ was purchased from Strem Chemicals, Inc. $Re(CO)_5OTf$,[2] *trans*-$Re(PPh_3)(CO)_4I$,[3] *trans*-$[(PPh_3)_2Re(CO)_4][BF_4]$,[4] $Ph_2P(CH_2)_2B(C_8H_{14})$,[5] $[(Ph_2P(CH_2)_2B(C_8H_{14}))_2Re(CO)_4][BF_4]$,[6] boroxycarbene **2-E$_2$**,[6] boroxymethylboroxycarbene [**3-E$_2$**]$^-$,[6] Cl-9-BBN,[7] Ph_2PCH_2Li,[8] $^tBu(CH_2)_2B(C_8H_{14})$,[9] $[Pt(dmpe)_2][PF_6]_2$ ([**Pt**][PF$_6$]$_2$),[10] and $NaBAr^F{}_4$[11] ($BAr^F{}_4$ = $[B(C_6H_3(3,5\text{-}(CF_3)_2)_4]$) were synthesized according to literature procedures. Elemental analyses were performed by Robertson Microlit Laboratories, Madison, NJ. ^1H and ^{13}C NMR spectra were recorded on Varian Mercury 300, 400-MR, INOVA-500 or -600 MHz spectrometers at room temperature, unless indicated otherwise. Chemical shifts are reported with respect to residual internal protio solvent for ^1H and $^{13}C\{^1H\}$ spectra. Other nuclei were referenced to an external standard: H_3PO_4 (^{31}P), 15% BF_3•$Et_2O/CDCl_3$ (^{11}B), $CFCl_3$ (^{19}F), all at 0 ppm. High resolution mass spectra (HRMS) were obtained at the California Institute of Technology Mass Spectrometry Facility.

X-ray Crystallography Procedures.

X-ray quality crystals were grown as indicated in the experimental procedures for each complex. The crystals were mounted on a glass fiber with Paratone-N oil. Structures were determined using direct methods with standard Fourier techniques using the Bruker AXS software package. In some cases, Patterson maps were used in place of the direct methods procedure. Full crystallographic details are provided in the section below.

II. Reductions of *trans*-$[(PPh_3)_2Re(CO)_4]^+$ ($[\mathbf{1\text{-}Ph_2}]^+$).

Synthesis of $[HPt(dmpe)_2][PF_6]$ ($[\mathbf{HPt}][PF_6]$).

While the published literature procedure is serviceable,[10] certain alterations improved the yield in our hands. In particular, the reaction was run more dilute to ensure that all $[\mathbf{HPt}]^+$ remained in solution, and the use of EtOH (which appeared to decompose $[\mathbf{HPt}]^+$ at a reasonably quickly) was avoided. A 500 mL round bottom flask was charged with 1.96 g (2.49 mmol) $[Pt(dmpe)_2][PF_6]_2$, 200 mL acetonitrile, and a stir bar. With the acetonitrile solution stirring, 0.189 g (4.99 mmol, 2 equiv) $NaBH_4$ (as a 10 wt% mixture in basic alumina) was added as a solid. The mixture was stirred for ~12 hours, filtered through a fine frit, and the filtrate was dried under vacuum to afford an off-white powder. The crude material contained only $[\mathbf{HPt}][PF_6]$ and excess $NaBH_4$. The desired $[\mathbf{HPt}][PF_6]$ was extracted with 15 mL C_6H_5Cl, and filtered away from the insoluble white $NaBH_4$. The solvent was removed from the filtrate under vacuum, and the very pale yellow solids were washed with 3 x 5 mL Et_2O to afford 1.414 g (88% yield) spectroscopically pure $[\mathbf{HPt}][PF_6]$. This procedure provided material with spectroscopic

characteristics that matched the published values well, and also matched samples of [**HPt**][PF_6] prepared using the literature procedure.

Reaction of [HPt][PF_6] with CD_2Cl_2.

A J-Young NMR tube was charged with 16 mg (0.0234 mmol) [**HPt**][PF_6] and ~0.5 mL CD_2Cl_2. The tube was sealed and monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy over 1 week. Colorless crystals of [**Pt**]Cl_2 formed in the tube over the course of the week, and spectroscopic analysis revealed steady disappearance of the hydride resonances of [**HPt**]$^+$ (-11.62, p, J_{PH} = 29.4 Hz, J_{PtH} = 705 Hz) with concomitant growth of a peak at 2.98 (pent, J_{HD} = 1.6 Hz) assigned to CHD_2Cl.

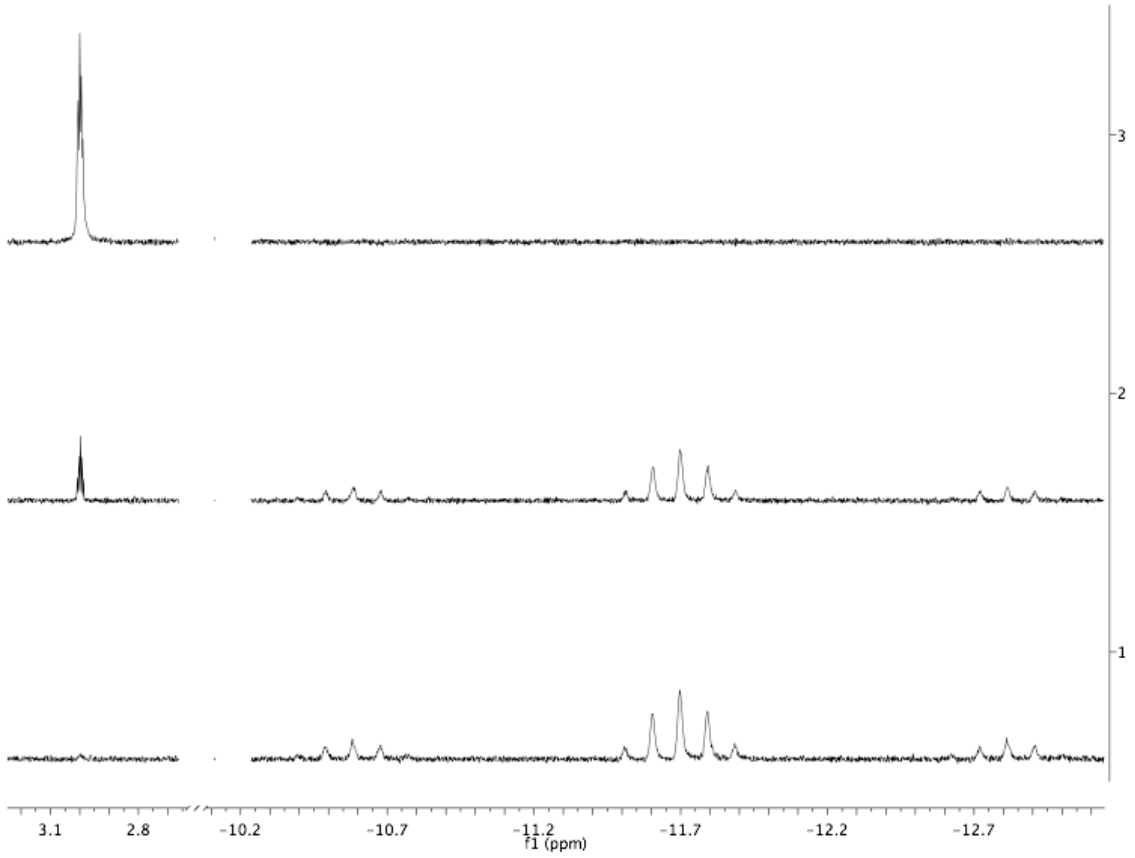


Figure S1. ^1H NMR time course (bottom, 1 h; middle, 12 h; top, 1 week):

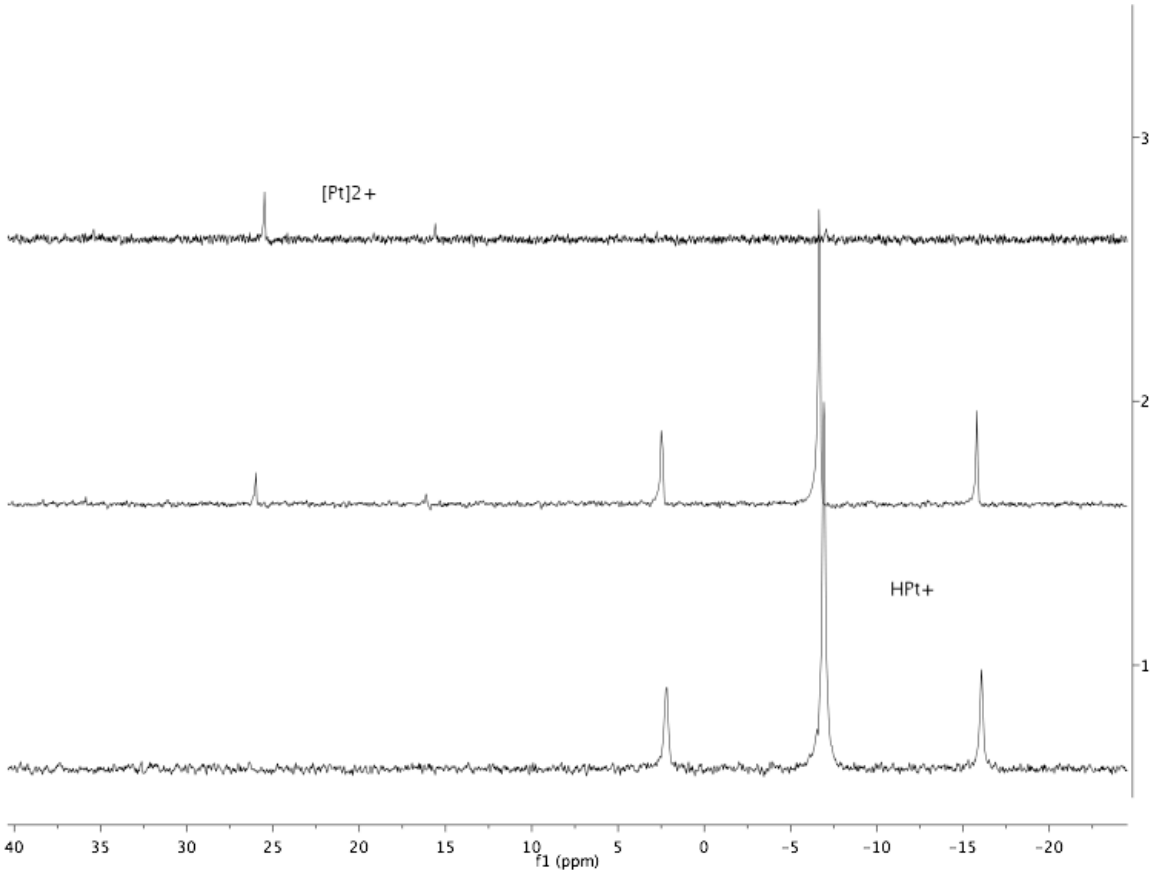


Figure S2. $^{31}P\{^{1}H\}$ NMR time course (bottom, 1 h; middle, 12 h; top, 1 week).

Reaction of [1-Ph$_2$][BF$_4$] with [HPt][PF$_6$].

A J-Young NMR tube was charged with 7.9 mg (0.0087 mmol) [**1-Ph$_2$**][BF_4], 5.6 mg (0.0087 mmol) [**HPt**]$^+$, and ~0.6 mL C_6D_5Cl. After 1 hour, a small resonance for formyl $(PPh_3)_2Re(CO)_3(CHO)$ (**2-Ph$_2$**) was observed at δ 15.22. After ~35 hours, a mixture of $(PPh_3)_2Re(CO)_3H$ and $(PPh_3)Re(CO)_4H$ was observed, which grew as the [**HPt**]$^+$ was consumed. The reaction was monitored for 7 days, during which time the formyl did not accumulate to any significant extent; eventually only the two Re-H species remained.

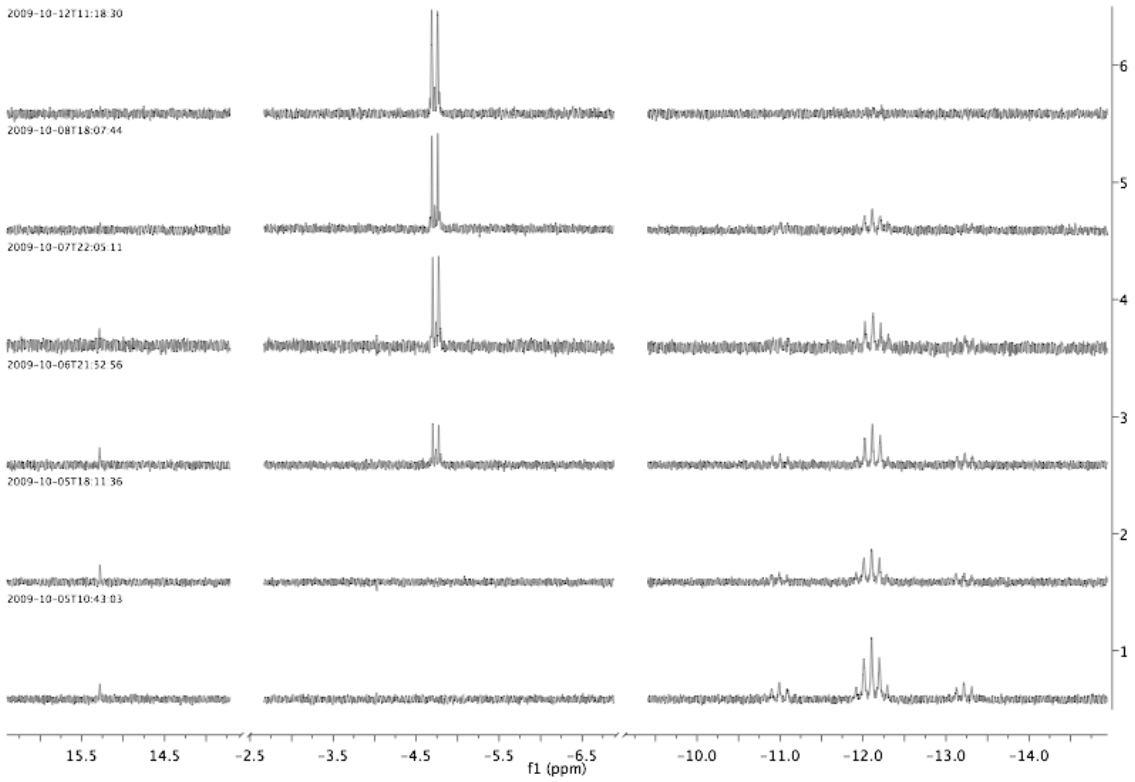


Figure S3. ^{1}H NMR timecourse.

Reaction of [1-Ph$_2$][BF$_4$] with [HPt][PF$_6$] in presence of B(OR)$_3$.

A ~0.6 mL C_6D_5Cl solution of 6.3 mg (0.0329 mmol) isopropyl pinacol borate was added to 10.9 mg (0.0169 mmol) [**HPt**][PF_6], and the solution was then added to 15.4 mg (0.0169 mmol) [**1-Ph$_2$**][BF_4]. The resulting slurry was added to a J-Young NMR tube, and monitored by ^{1}H and ^{31}P NMR. The reaction proceeded slowly, with small amounts of formyl persisting over the course of 6 days and large amounts of Re-H species being formed. Significant variation in the ratio of Re hydride species formed was observed in multiple experiments. The rate of the reaction was roughly the same as that with no added acid (Figure S5).

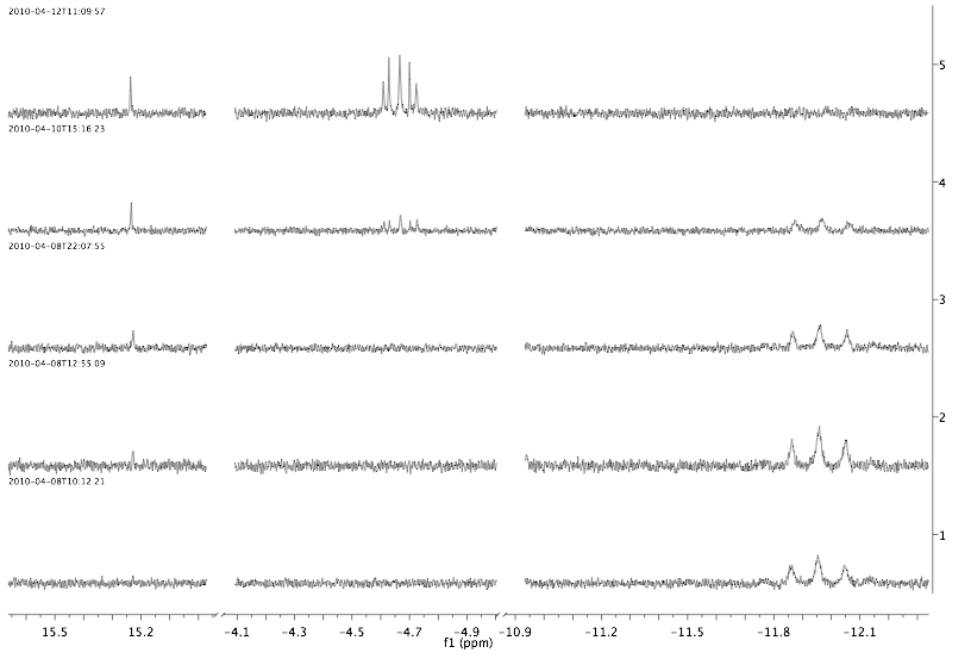


Figure S4. ^{1}H NMR timecourse.

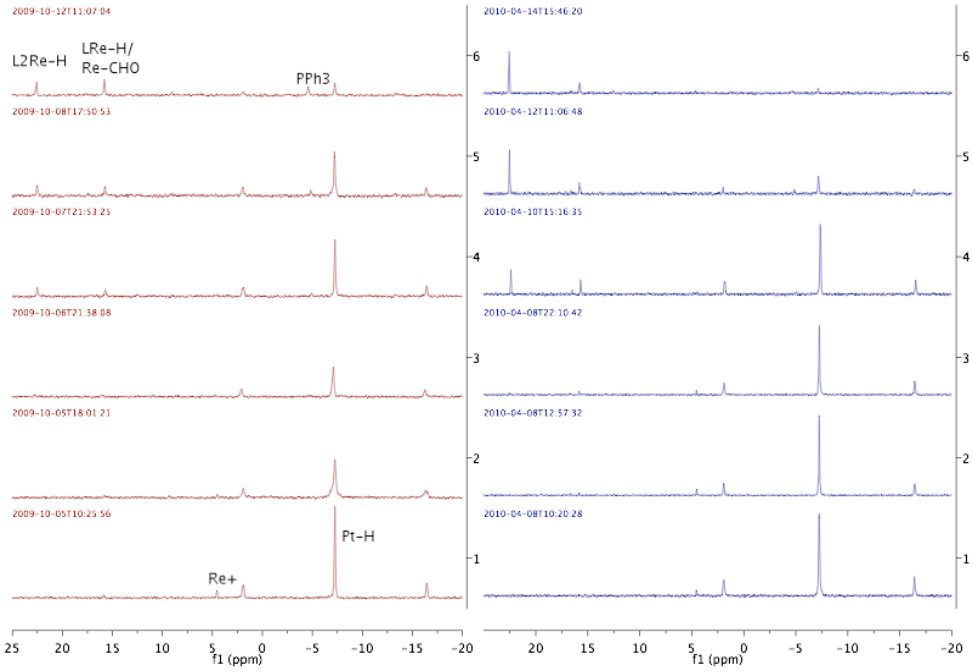


Figure S5. ^{31}P{^{1}H} NMR. Comparison of no added Lewis acid added (left) and trialkylborate (right).

Reaction of [1-Ph_2][BF_4] with [HPt][PF_6] in presence of $B(C_6F_5)_3$.

A vial was charged with 17.9 mg (0.0197 mmol) [**1-Ph_2**][BF_4], 10.1 mg (0.0197 mmol) $B(C_6F_5)_3$, and 12.6 mg (0.0197 mmol) [**HPt**][PF_6]. C_6D_5Cl (~0.6 mL) was added to the vial, and the slurry was moved to a J-Young NMR tube, where it was shaken well. NMR spectroscopy revealed complete consumption of [**HPt**]$^+$ and small amounts of [**Pt**]$^{2+}$ in solution (with the majority precipitating), affording only one Re-containing species, assigned as $[(PPh_3)_2Re(CO)_4][HB(C_6F_5)_3]$. The same reactivity was observed when 2 equiv $B(C_6F_5)_3$ were added. **^{1}H NMR** (C_6D_5Cl, 300 MHz): δ 7.19-7.29 (m, 12H), 7.32-7.40 (m, 8H). **^{31}P{^{1}H} NMR** (C_6D_5Cl, 121 MHz): δ 4.2. **^{19}F NMR** (C_6D_5Cl, 282 MHz): δ -134.19 (m, 6F), -161.32 (t, J_{FF} = 20.5 Hz, 3F), -165.77 (m, 6F). **^{11}B NMR** (C_6D_5Cl, 160 MHz): with 2 equiv added $B(C_6F_5)_3$, δ ~ 0 (br), consistent with exchange between $B(C_6F_5)_3$ and $[HB(C_6F_5)_3]^-$. **IR** (C_6D_5Cl): ν_{CO} 2003 (s); ν_{BH} 1644 (m), ν_{CF} 1514 (m), 1466 (s).

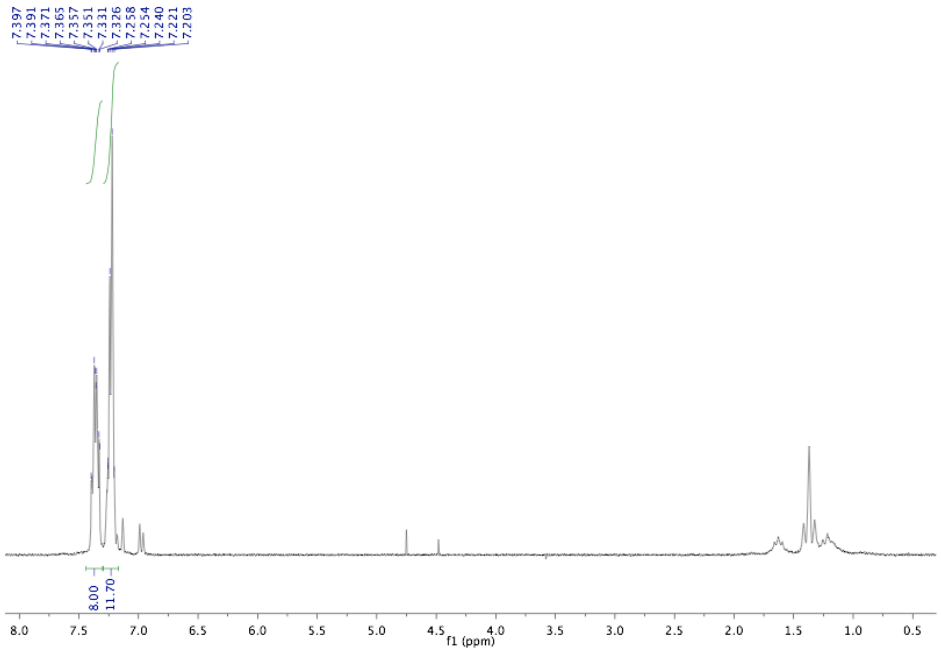


Figure S6. ^{1}H NMR.

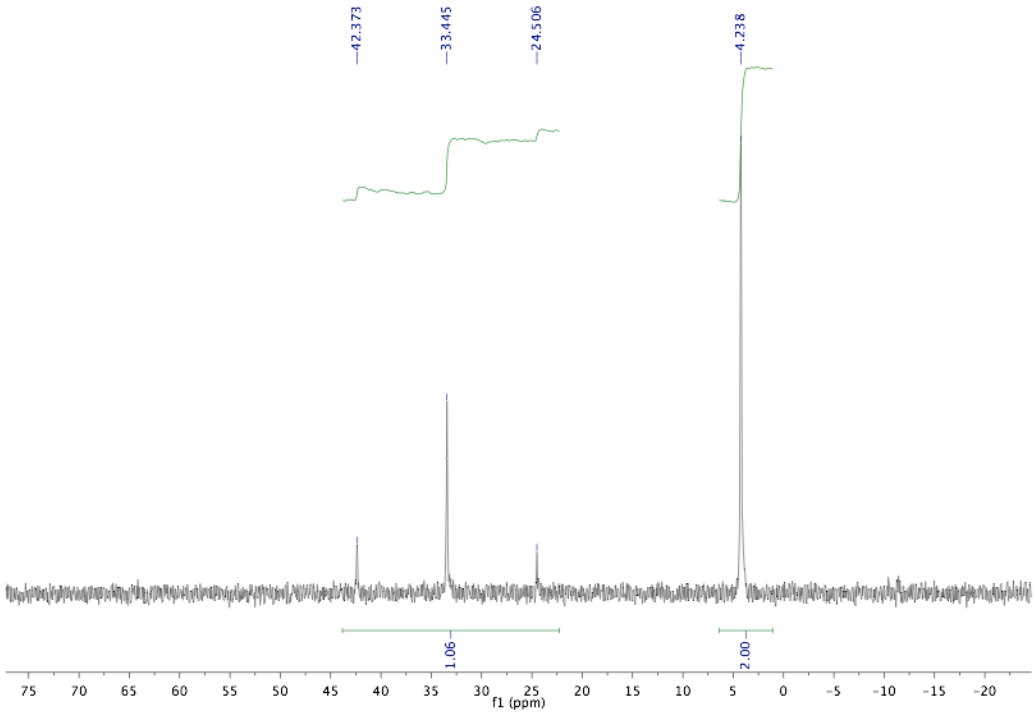


Figure S7. $^{31}P\{^{1}H\}$ NMR (peak at 33.4 with Pt satellites is residual [**Pt**]$^{2+}$.

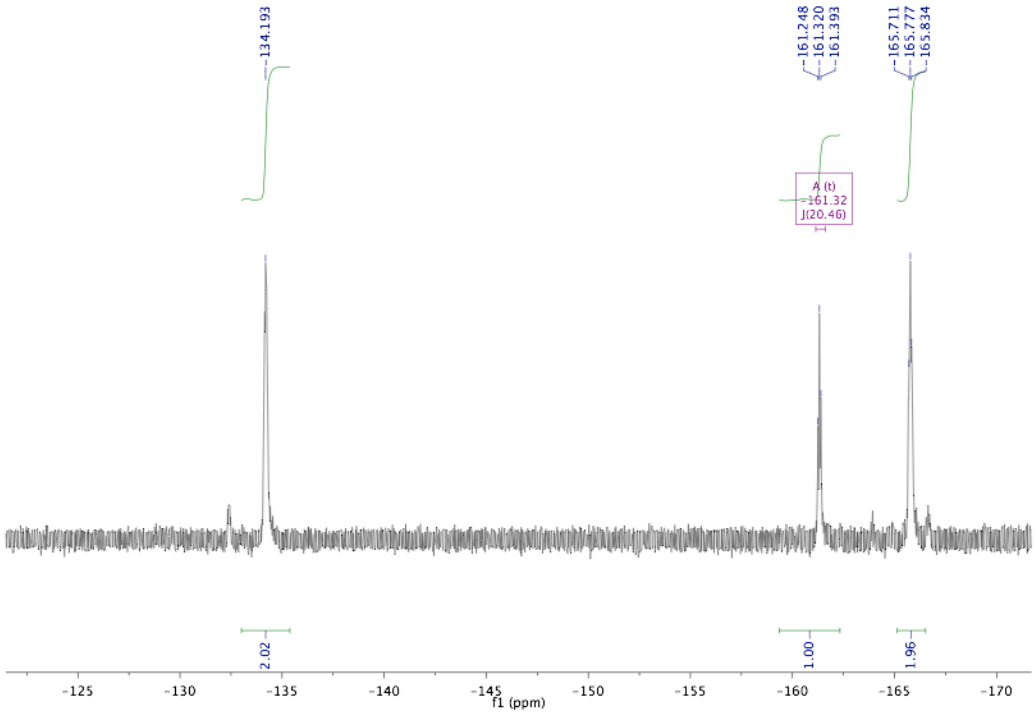


Figure S8. ^{19}F NMR.

NMR Scale Reaction of [1-Ph_2][BF_4] with [HPt][PF_6] in presence of trialkylborane.

A ~0.6 mL C_6D_5Cl solution of 6.3 mg (0.0300 mmol) ^{t}BuCH$_2$CH$_2$B(C_8H_{14}) was added to 9.7 mg (0.00152 mmol) [**HPt**][PF_6], and the mixture was added to 13.8 mg (0.0152 mmol) solid [**1-Ph_2**][BF_4]. The reaction mixture was transferred to a J-Young NMR tube, and monitored by multinuclear NMR. After 15 minutes, high conversion to a boroxycarbene species (δ 14.60) was observed; the reaction was complete within 3 hours. NMR parameters of the ~2:1 mixture of ^{t}BuCH$_2$CH$_2$B(C_8H_{14}) : **2-Ph_2** (reversible adduct formation leads to chemical shifts dependent on the amount of borane present). The product displayed spectral parameters very similar to the product of reduction of [**1-Ph_2**][BF_4] with 1 equiv $NaHBEt_3$ (1.0 M in toluene). **^{1}H NMR** (C_6D_5Cl, 300 MHz): δ 0.91 (s, ^{t}*Bu*CH$_2$CH$_2$B(C_8H_{14}), 18H), 1.15-1.38 (m, ^{t}BuCH$_2$CH$_2$B(C_8*H*$_{14}$), 16H), 1.59 (br m, ^{t}BuCH$_2$C*H*$_2$B(C_8H_{14}), 4H), 1.65-1.95 (m, ^{t}BuC*H*$_2$CH$_2$B(C_8*H*$_{14}$), 24H), 7.07-7.21 (m, PPh_3, 12H), 7.58-7.64 (m, PPh_3, 8H), 14.60 (s, Re-CHO, 1H). **^{31}P{^{1}H} NMR** (C_6D_5Cl, 121 MHz): δ 14.5.

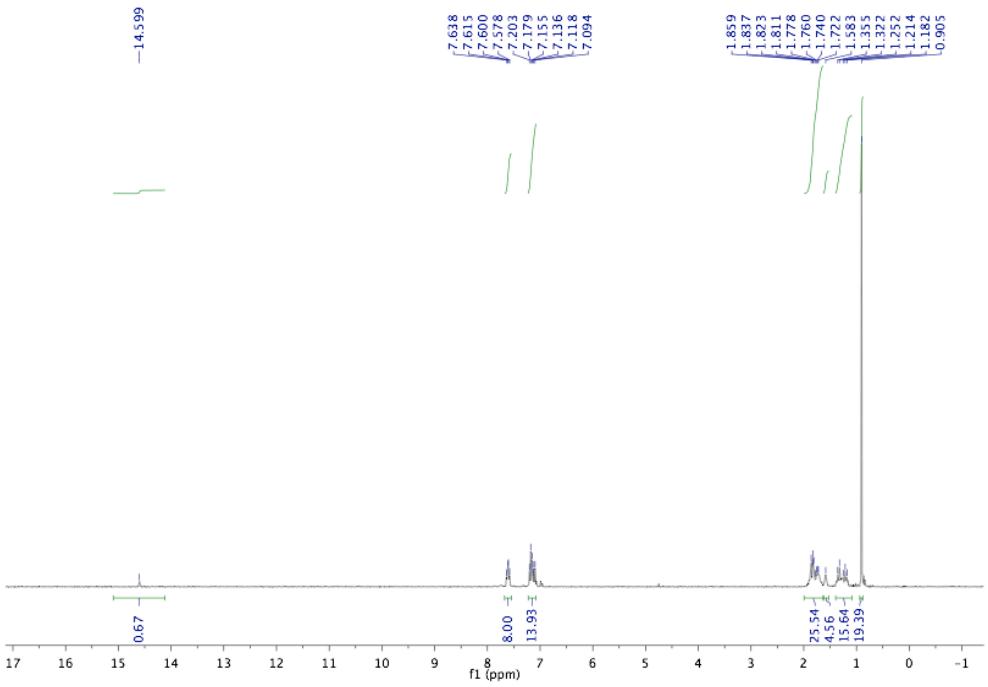


Figure S9. ^{1}H NMR.

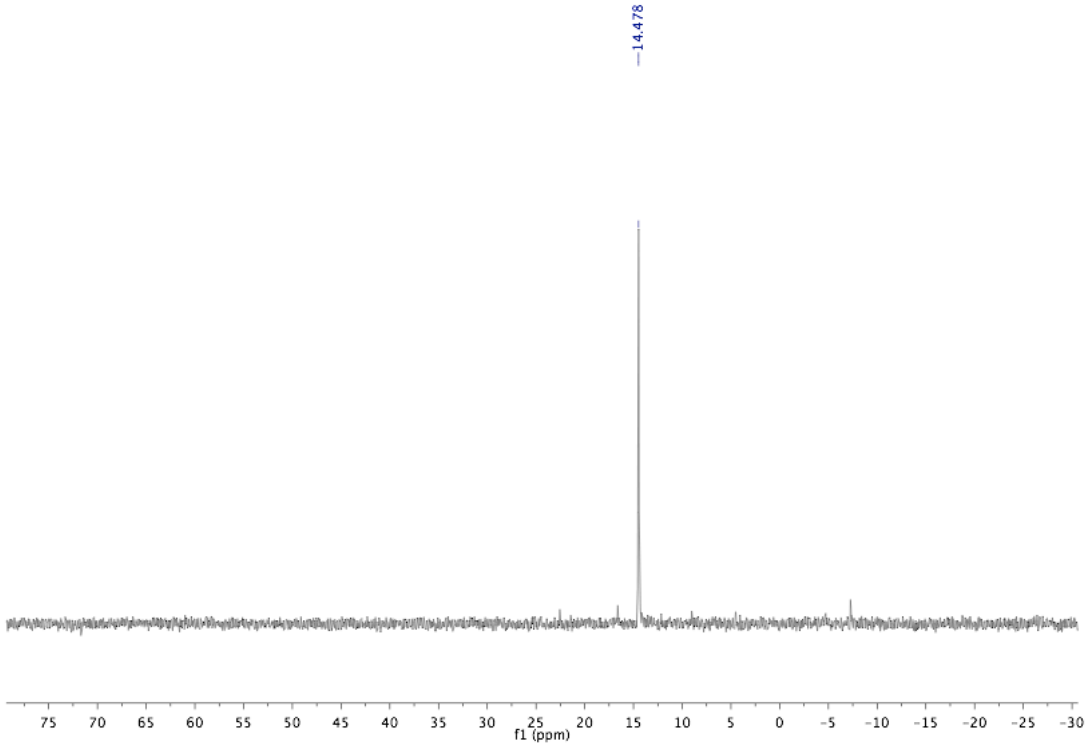


Figure S10. $^{31}P\{^{1}H\}$ NMR:

Synthesis of *mer,trans*-$(PPh_3)_2Re(CO)_3(CHO)$ (2-Ph_2).

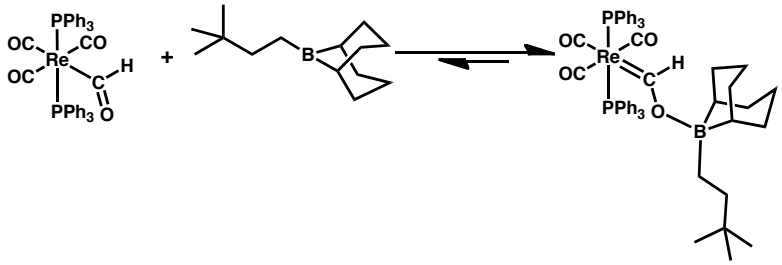
An alternative route was followed: a 20 mL scintillation vial was charged with 95 mg (0.083 mmol) *trans*-$[(PPh_3)_2Re(CO)_4][BPh_4]$ and 5 mL THF. With stirring, 83 μL (0.083 mmol) $LiHBEt_3$ (1.0 M in THF) was added dropwise, during which time the colorless solution turned yellow. The reaction was stirred for 5 minutes, filtered, and the solvents concentrated to 1 mL under vacuum. A layer of 2 mL pentane was added, and the mixture placed in the freezer at -35 °C. A yellow powder formed overnight, which contained a mixture of **2-Ph_2** and $LiBPh_4$. Another 10 mL pentane was added to the mother liquor of the first crystallization, which upon cooling yielded a second crop of powder, which yielded ~30 mg pure **2-Ph_2** (45% yield). As previously reported, the product reacts with CH_2Cl_2 and was sparingly soluble in most solvents; an IR spectrum (KBr/nujol mull) matched the literature values well.[4]

Single crystals of the BEt_3 adduct **2-Ph_2**•BEt_3 were obtained in a separate reaction by adding 10 equiv BEt_3 (1.0 M in hexanes) to a THF solution of **2-Ph_2** (prepared as above), which was then layered 1:1 with pentane and cooled to -35 °C. Long colorless needles suitable for XRD needles grew over a few days. See below for full crystallographic details.

Titration of 2-Ph_2 with ^{t}Bu$(CH_2)_2B(C_8H_{14})$.

The equilibrium constant for adduct formation between formyl **2-Ph_2** and a ^{t}Bu$(CH_2)_2B(C_8H_{14})$ (Scheme S1) was carried out by titration, with monitoring by ^{1}H NMR. Due to the insolubility of **2-Ph_2**, an internal standard was used to quantify the concentration. A sample of 15.2 mg (0.0185 mmol) was weighed and 0.6 mL THF-d_8 was added. The slurry was filtered into a J-Young NMR tube, and a 2.8 mg crystal (0.0106 mmol) 18-crown-6 was added to the tube. An initial NMR

spectrum showed 1.01:1.00 18-crown-6:formyl, and the concentration of Re was determined to be 17.5 mM. Aliquots of a 1.0 M solution of ^{t}Bu(CH$_2$)$_2$B(C$_8$H$_{14}$) in THF-d_8 were then added: 0.13, 0.33, 0.89, 1.33, and 1.68 equiv. The chemical shift change of the formyl was recorded at each concentration of borane, and a Benesi-Hildebrand-type analysis[12] gave a linear plot of 1/Δδ vs. 1/[^{t}Bu(CH$_2$)$_2$B(C$_8$H$_{14}$)] (Figure S11), providing an estimate of the equilibrium constant of Scheme S1, K_{eq} = 100 M^{-1} favoring adduct formation. A correction was made for the background equilibrium of THF binding the borane, as less borane would be available to interact with the formyl.



Scheme S1.

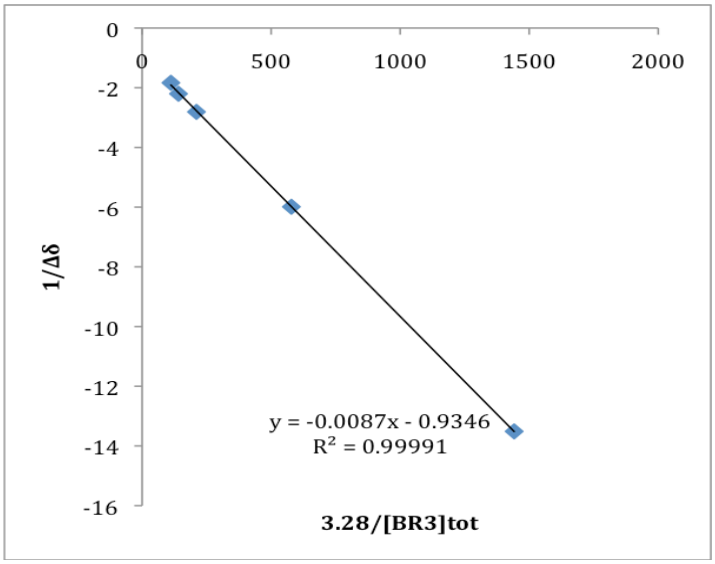


Figure S11. Benesi-Hildebrand plot.

III. Synthesis of Complexes with Pendent Boranes.

Synthesis of Crude $Ph_2PCH_2B(C_8H_{14})$.

A slurry of 1.42 g (6.87 mmol) Ph_2PCH_2Li in 50 mL pentane was frozen in the cold well of a glovebox. As the slurry thawed, a thawing 20 mL pentane solution of Cl-9-BBN was added. The mixture was allowed to warm with stirring, and was stirred for 18 hours. White solids remained throughout the reaction, which were collected on a frit, and washed with 3 x 5mL THF. The solids were dried, giving 1.97 g (6.15 mmol, 90%) of white powder assigned as oligomeric $Ph_2PCH_2B(C_8H_{14})$. These solids are insoluble in common organic solvents. The crude phosphinoborane ligand could be used at this stage, but better results were obtained when the ligand was treated successively with pyridine and BF_3•Et_2O, as follows.

Synthesis of $Ph_2PCH_2B(C_8H_{14})$• pyridine.

A 20 mL scintillation vial was charged with 0.756 g (2.36 mmol) $Ph_2PCH_2B(C_8H_{14})$, in the form of crude white insoluble solids as described above. A stirbar and 10 mL toluene was added, giving a thick white slurry. A 5 mL toluene solution of 0.242 g (3.07 mmol) pyridine was added, and over a few minutes the slurry steadily became less cloudy, although there were still some solids that did not dissolve over the course of the reaction. After 6 hours, the cloudy reaction mixture was filtered, and the filtrate evaporated to dryness *in vacuo*. The white solids where washed with 3 x 4 mL pentane, and dried to give 0.700 g (1.75 mmol, 74%) white microcrystalline $Ph_2PCH_2B(C_8H_{14})$•pyridine. The pyridine adduct was soluble in most organic solvents (except pentane). **^{1}H NMR** (THF-d_8, 500 MHz): δ 1.14-1.25 (m, 3H, $Ph_2PCH_2B(C_8H_{14})$), 1.38 (d, J_{PH} = 4.7 Hz, 2H, $Ph_2PCH_2B(C_8H_{14})$), 1.38-1.44 (m, 2H,

$Ph_2PCH_2B(C_8H_{14})$), 1.60 (m, 3H, $Ph_2PCH_2B(C_8H_{14})$), 1.73-1.79 (m, 2H, $Ph_2PCH_2B(C_8H_{14})$), 1.90 (m, 2H, $Ph_2PCH_2B(C_8H_{14})$), 2.16 (br m, 2H, $Ph_2PCH_2B(C_8H_{14})$), 7.07 (m, 6H, $Ph_2PCH_2B(C_8H_{14})$), 7.20 (m, 4H, $Ph_2PCH_2B(C_8H_{14})$), 7.35 (t, J_{HH} = 7.0 Hz, 2H, *m*-C_5H_5N), 7.75 (t, J_{HH} = 7.6 Hz, 1H, *p*-C_5H_5N), 8.45 (d, J_{HH} = 5.2 Hz, 2H, *o*-C_5H_5N). **$^{31}P\{^1H\}$ NMR** (THF-d_8, 121 MHz): δ -17.1. **^{11}B NMR** (THF-d_8, 160 MHz): δ -0.2. **$^{13}C\{^1H\}$ NMR** (THF-d_8, 125 MHz): δ 23.30 (br), 25.57, 25.84, 31.24, 33.35, 126.29 (*m*-C_5H_5N), 127.97 (*p*-Ph), 128.53 (d, $^3J_{PC}$ = 6.3 Hz, *m*-Ph), 133.45 (d, $^2J_{PC}$ = 19.2 Hz, *o*-Ph), 140.57 (*p*-C_5H_5N), 144.86 (d, $^1J_{PC}$ = 18.2 Hz, *ipso*-Ph), 146.57 (*o*-C_5H_5N). **HRMS** (FAB^+): m/z calcd. for $C_{26}H_{31}BNP$: 399.2287. Found: 399.2284 (M^+), 320.1907 (M-C_5H_5N), 200.1611 (M-Ph_2PCH_2).

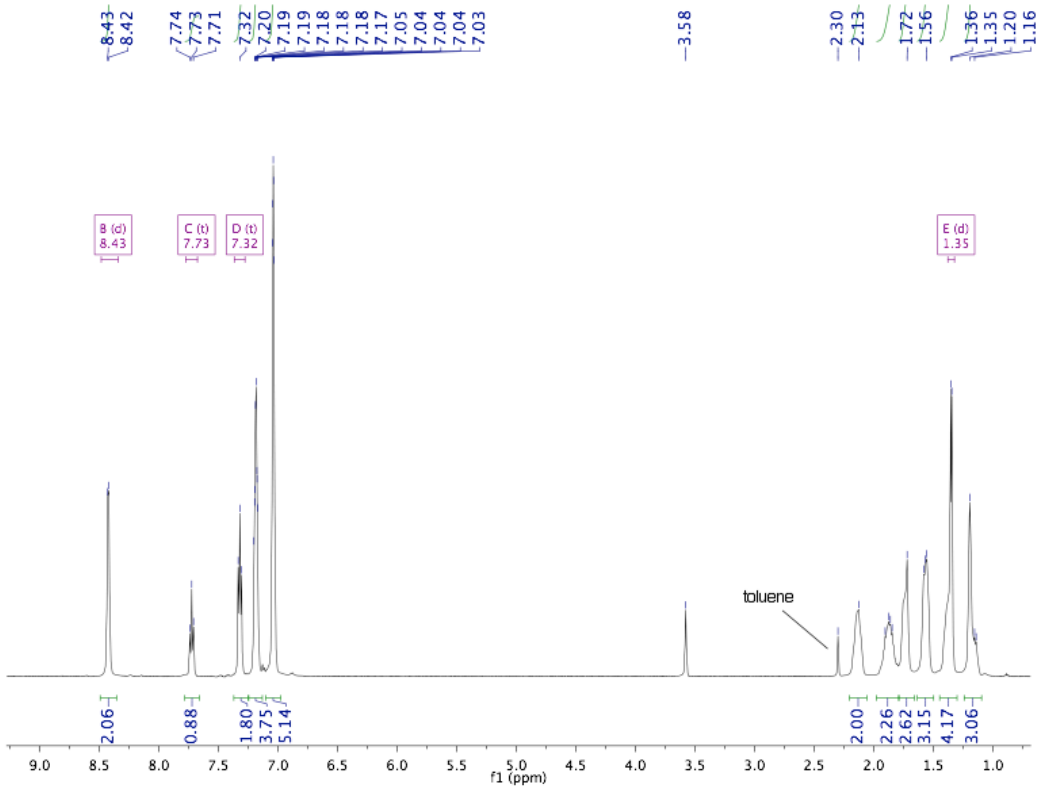


Figure S12. ^1H NMR (~3% residual toluene).

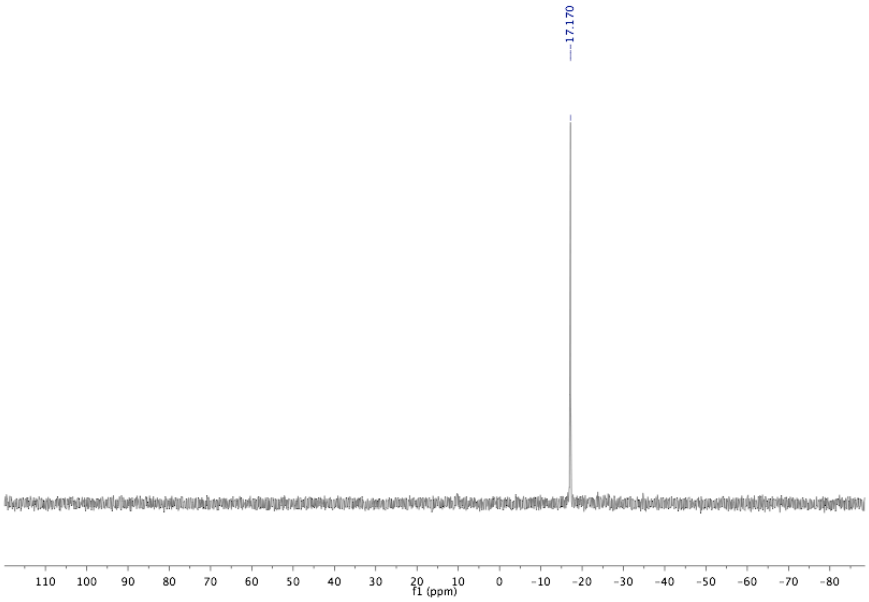


Figure S13. $^{31}P\{^{1}H\}$ NMR.

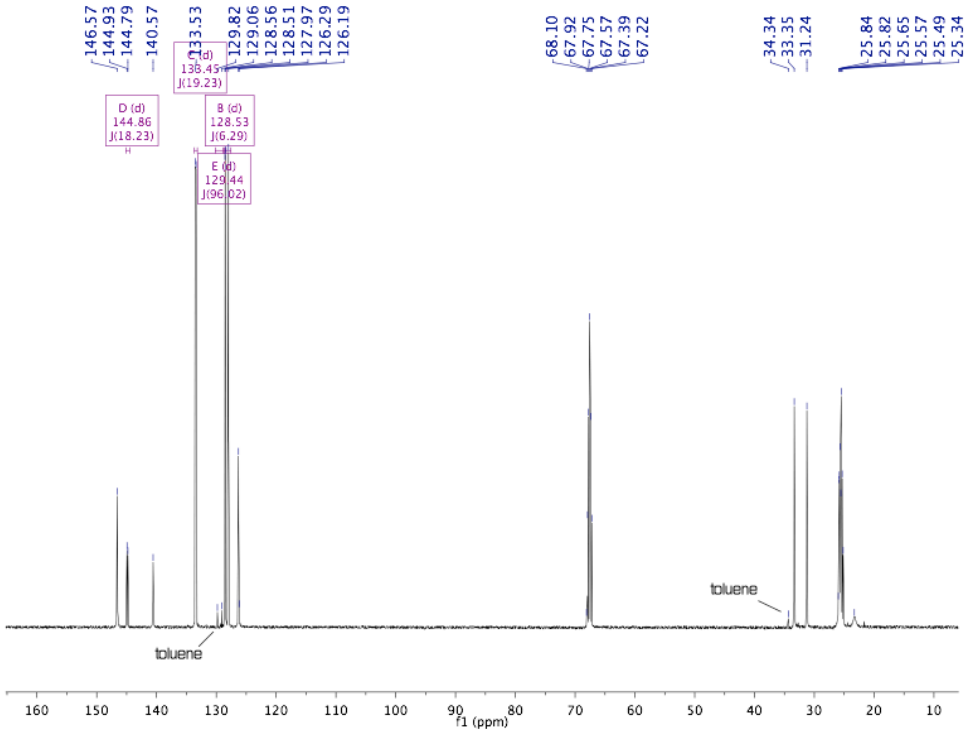


Figure S14. $^{13}C\{^{1}H\}$ NMR (~3% residual toluene).

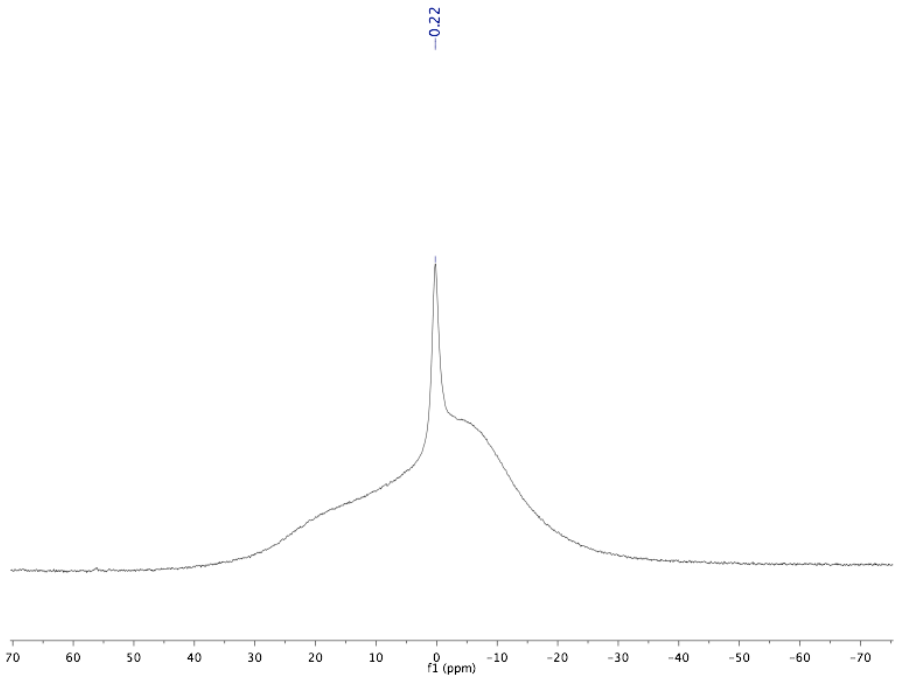


Figure S15. $^{11}B\{^{1}H\}$ NMR (broad underlying signal is borosilicate in probe construction).

Synthesis of $Ph_2PCH_2B(C_8H_{14})$:

A 20 mL scintillation vial was charged with 615 mg (1.5 mmol) $Ph_2PCH_2B(C_8H_{14})$•pyridine, 18 mL Et_2O, and a stirbar. With stirring, 195 µL BF_3•OEt_2 was added dropwise by syringe. As the BF_3•OEt_2 was added, fluffy white precipitates formed, eventually giving a thick white slurry. After stirring for 20 minutes, the solids were collected on a frit, and washed with 3 x 5 mL Et_2O, and 4 x 4 mL CH_2Cl_2, yielding 369 mg (1.15 mmol, 77%) $Ph_2PCH_2B(C_8H_{14})$. This material was quite insoluble, precluding full characterization, but yielded clean metallation reactions. Anal. Calcd. for $C_{21}H_{26}BP$: C, 78.77; H, 8.18. Found: C, 78.52; H, 8.45.

Synthesis of *mer,trans*-$(Ph_2PCH_2B(C_8H_{14}))_2Re(CO)_3Br$.

A pressure vessel equipped with a Teflon valve was charged with 1.33 g (4.16 mmol, 2 equiv) $Ph_2PCH_2B(C_8H_{14})$, 0.85 g (2.08 mmol, 1 equiv) $Re(CO)_5Br$, 30 mL toluene, and a stirbar. The

vessel was sealed and heated to 120 °C with stirring. The two mostly-insoluble white powders dissolved quickly upon heating, and the solution turned pale yellow as the reaction proceeded. After 18 hours, the reaction mixture was cooled and degassed under vacuum. After backfilling with argon the vessel was sealed and re-heated to 120 °C. After 4 days the mixture was cooled, degassed, put under argon, and re-heated again. After heating for another 48 hours, the reaction mixture was allowed to cool, and the solvents were removed to dryness, yielding 2.2 g crude product (90% pure by NMR). The crude material was purified by crystallization from a toluene/pentane mixture at -35 °C. **^{1}H NMR** (CD_2Cl_2, 500 MHz): δ 1.21-1.29 (m, 8H, $Ph_2PCH_2B(C_8H_{14})$), 1.64-1.84 (br m, 20H, $Ph_2PCH_2B(C_8H_{14})$), 2.94 (m, 4H, $Ph_2PCH_2B(C_8H_{14})$), 7.35-7.43 (m, 12H, Ph), 7.65 (m, 8H, Ph). **^{31}P{^{1}H} NMR** (C_6D_5Cl, 121 MHz): δ 8.2. **^{13}C{^{1}H} NMR** (CD_2Cl_2, 126 MHz): δ 24.08 ($Ph_2PCH_2B(C_8H_{14})$), 27.05 (br t, ($Ph_2PCH_2B(C_8H_{14})$), 32.34 (br, ($Ph_2PCH_2B(C_8H_{14})$), 34.72 ($Ph_2PCH_2B(C_8H_{14})$), 128.81 (m, (*m*-$Ph_2PCH_2B(C_8H_{14})$), 130.33 ((*p*-$Ph_2PCH_2B(C_8H_{14})$), 132.47 (m, (*o*-$Ph_2PCH_2B(C_8H_{14})$), 139.04 (m, (*ipso*-$Ph_2PCH_2B(C_8H_{14})$), 192.77 (t, J_{PC} = 8.5 Hz, CO), 192.87 (t, J_{PC} = 6.8 Hz, CO). **^{11}B NMR** (CD_2Cl_2, 160 MHz): δ 67.8 (v br). **IR** (CD_2Cl_2): 2012 (w), 1958 (vs), 1899 (s) cm^{-1}. **Anal. Calcd.** for $C_{45}H_{52}B_2BrO_3P_2Re$: C, 54.56; H, 5.29. Found: C, 54.39; H, 5.05.

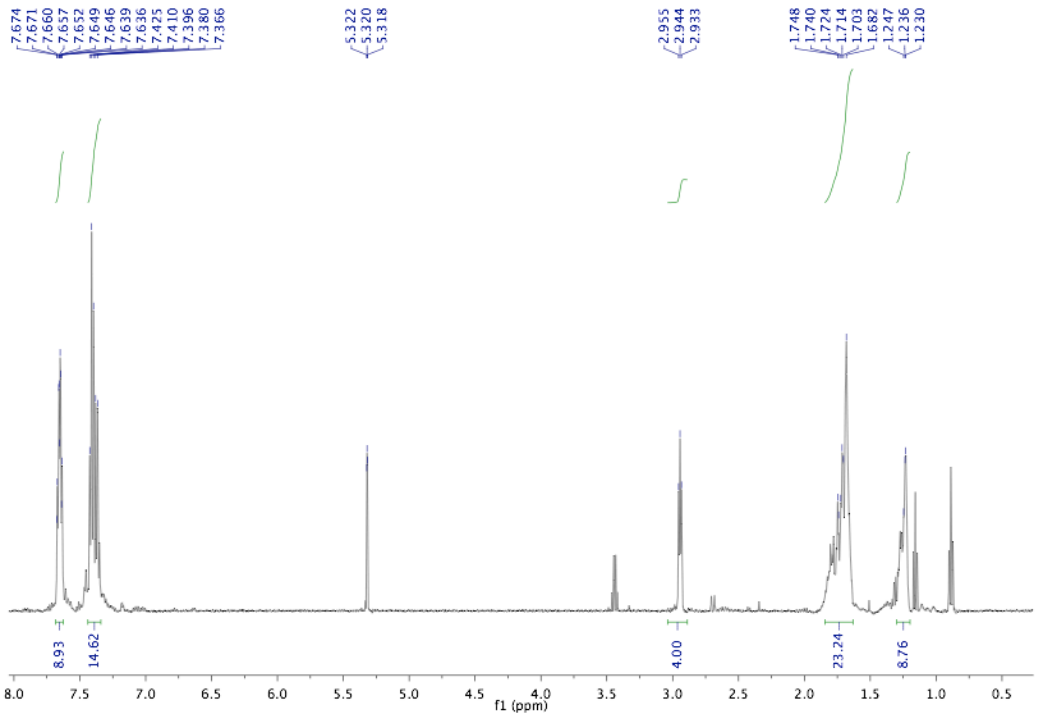


Figure S16. ^{1}H NMR.

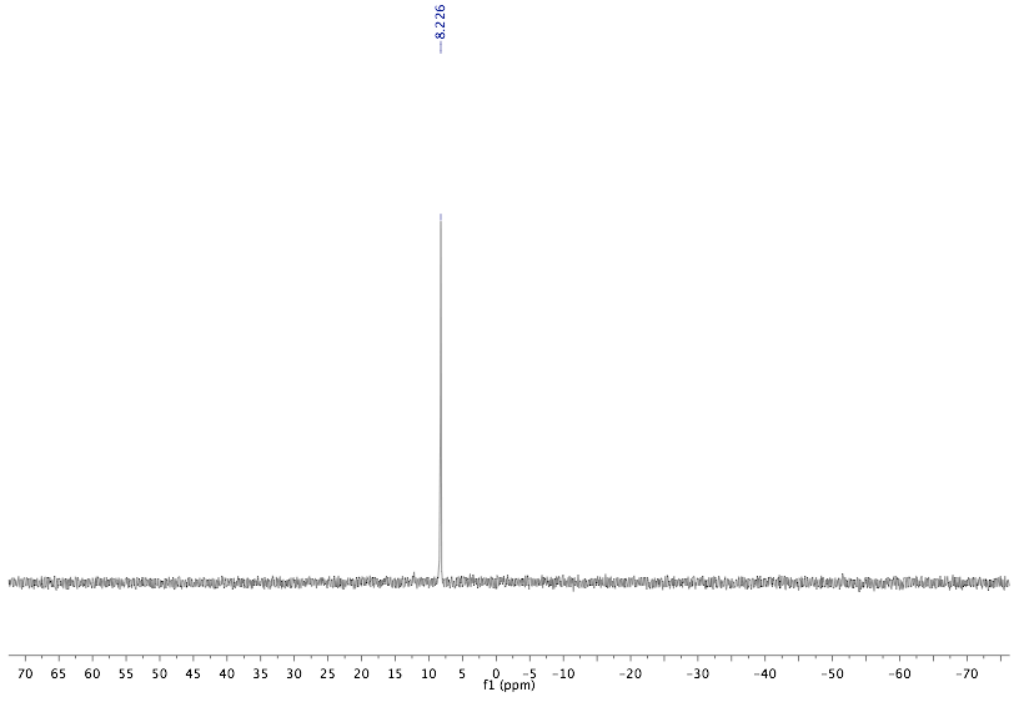


Figure S17. $^{31}P\{^{1}H\}$ NMR.

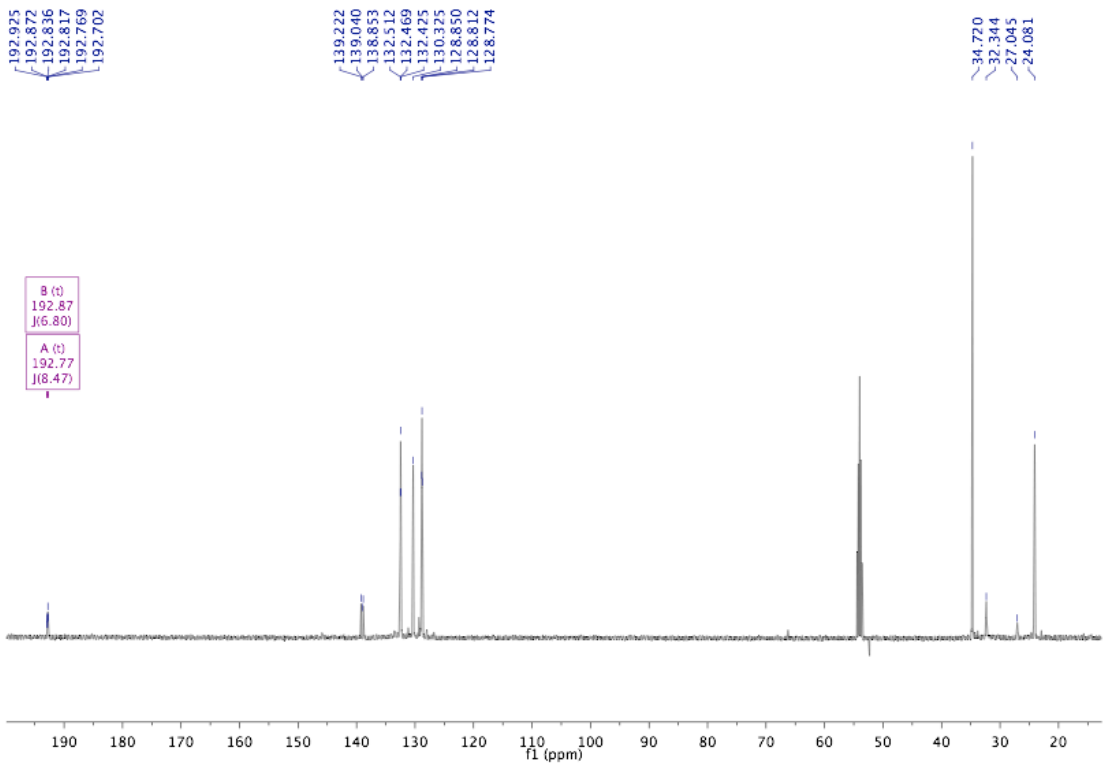


Figure S18. $^{13}C\{^{1}H\}$ NMR.

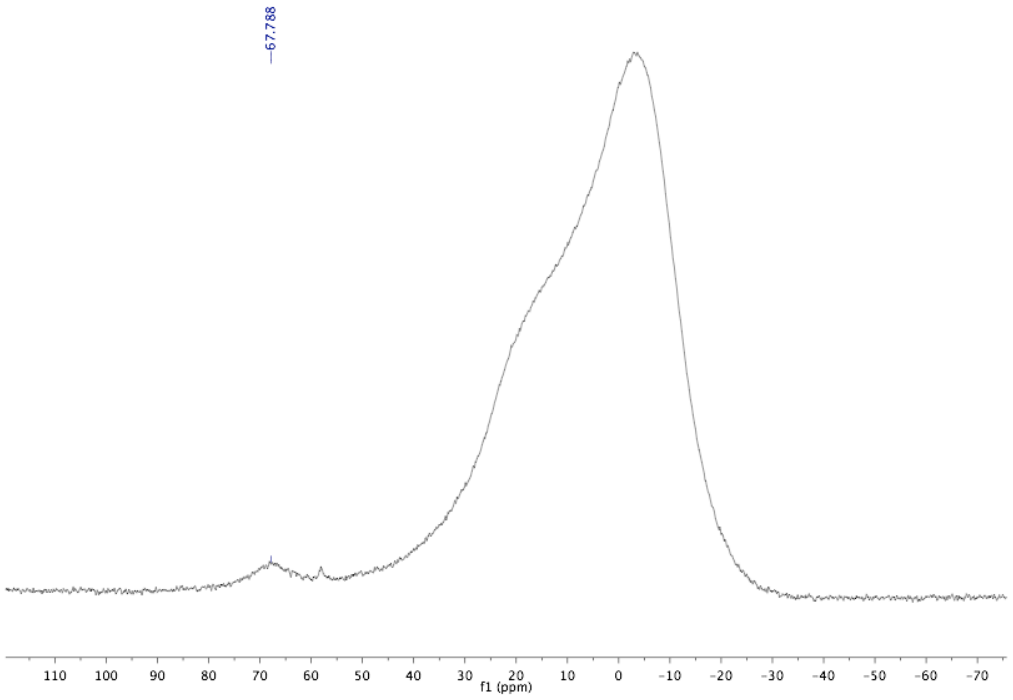


Figure S19. ^{11}B NMR.

Synthesis of *trans*-[$(Ph_2PCH_2B(C_8H_{14}))_2Re(CO)_4$][$B(C_6F_5)_4$] ([1-$M_2$][$B(C_6F_5)_4$]).

A 20 mL scintillation vial was charged with 0.145 g (0.157 mmol) [Ph_3C][$B(C_6F_5)_4$] and 5 mL C_6H_5Cl. To the stirring solution was added 25.1 μL (0.157 mmol) Et_3SiH dropwise. The orange-brown mixture was stirred for 25 minutes, after which time the mixture was added to a 60 mL Teflon-stoppered pressure vessel charged with a suspension of 0.156 g (0.157 mmol) *mer,trans*-$(Ph_2PCH_2B(C_8H_{14}))_2Re(CO)_3Br$ in 5 mL C_6H_5Cl. The vessel was sealed, removed from the box, and the contents frozen in a liquid nitrogen bath. After two freeze-pump-thaw cycles, 1 atm CO gas (treated by passage through a column of activated Mn oxide and sieves) was introduced to the vessel. The reaction vessel was sealed and stirred overnight. After ~12 hours, the mixture had a lighter, more yellow color. At this time the vessel was degassed, and the solvents were concentrated *in vacuo* to 2 mL. Treatment with 10 mL pentane prompted immediate precipitation of copious amounts of pale yellow solids. After stirring a few hours, the solids were collected on a frit, and washed with more pentane. The solids were dried, affording 0.228 g (90%, 0.141 mmol) spectroscopically pure [**1-M_2**][$B(C_6F_5)_4$]. X-Ray quality crystals were obtained by crystallization from 1,2-dichloroethane / pentane mixtures. **^{1}H NMR** (CD_2Cl_2, 500 MHz): δ 0.95 (m, 4H), 1.35-1.43 (m, 8H), 1.48 (br, 4H), 1.63-1.75 (m, 12H), 3.24 (m, 4H), 7.54 (s, 20H). **^{31}P{^{1}H} NMR** (CD_2Cl_2, 202 MHz): δ -13.7. **^{13}C{^{1}H} NMR** (CD_2Cl_2, 125 MHz): δ 22.97, 31.51 (br), 34.00, 35.48, 124.5 (v. br, *ipso*-C_6F_5), 130.07 (t, J_{PC} = 5.3 Hz, *m*-Ph), 131.62 (t, J_{PC} = 5.6 Hz, *o*-Ph), 132.44 (t, J_{PC} = 1.0 Hz, *p*-Ph), 135.27 (dd, J_{PC} = 25.9, 26.7 Hz, *ipso*-Ph), 136.88 (dm, J_{PF} = 241.4 Hz), 138.82 (dm, J_{PF} = 245.7 Hz), 148.74 (dm, 239.1 Hz), 186.37 (t, J_{PC} = 7.4 Hz). **^{11}B NMR** (CD_2Cl_2, 160 MHz): δ 88.6 (br), -16.8 (BAr^F_4). **IR** (C_6D_5Cl): 1998 cm^{-1}. **HRMS** (TOF ES^+): m/z calcd for $C_{46}H_{52}B_2O_4P_2Re$: 939.3102. Found: 939.3076.

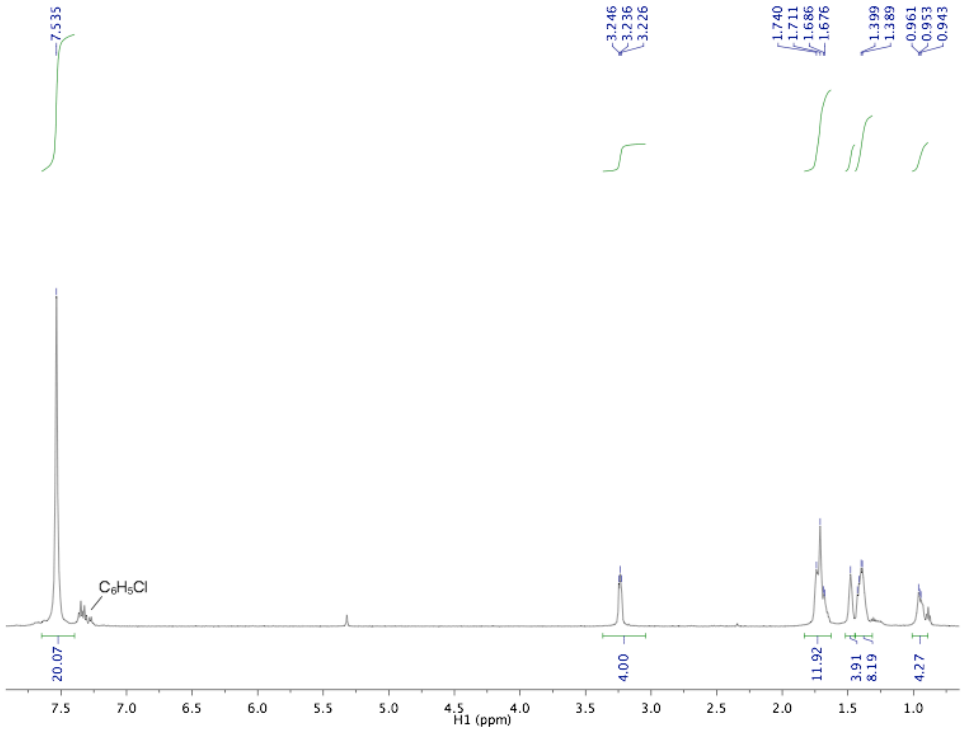


Figure S20. ^{1}H NMR.

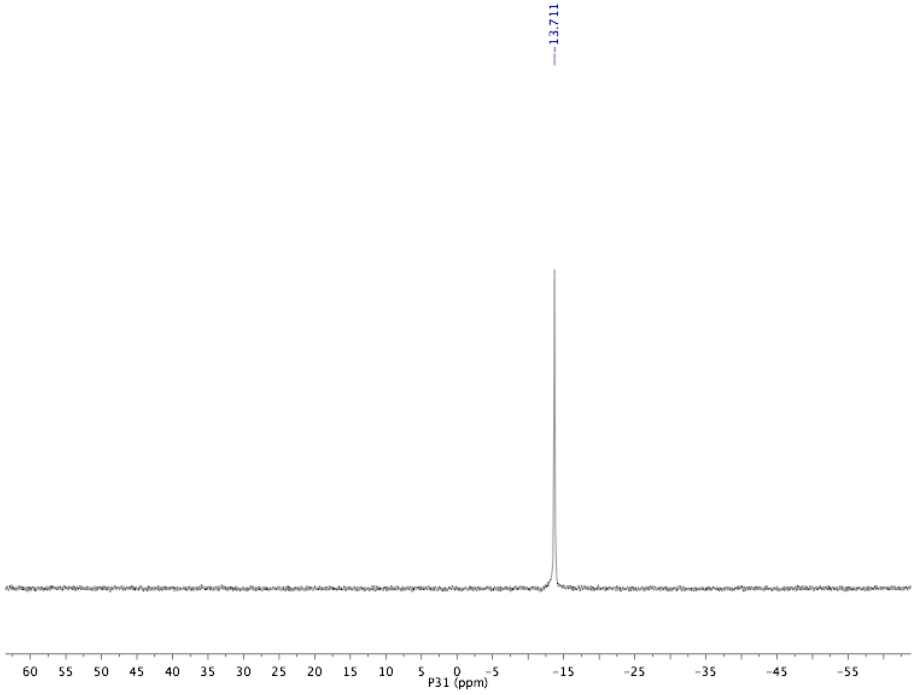


Figure S21. $^{31}P\{^{1}H\}$ NMR.

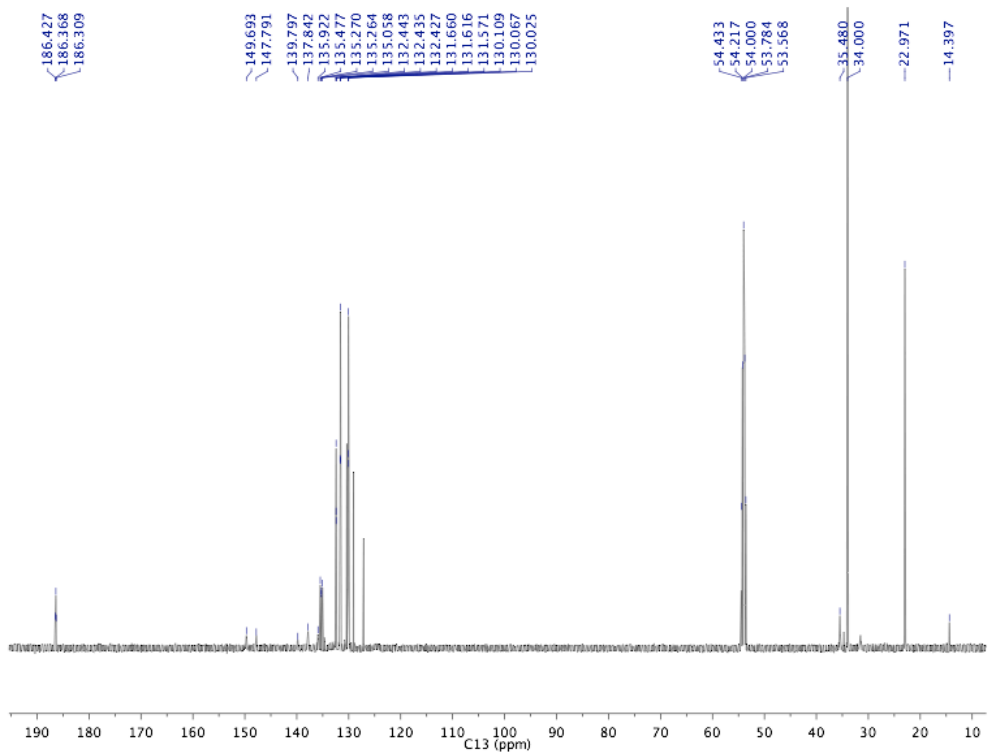


Figure S22. $^{13}C\{^{1}H\}$ NMR (~0.5 equiv C_6H_5Cl present).

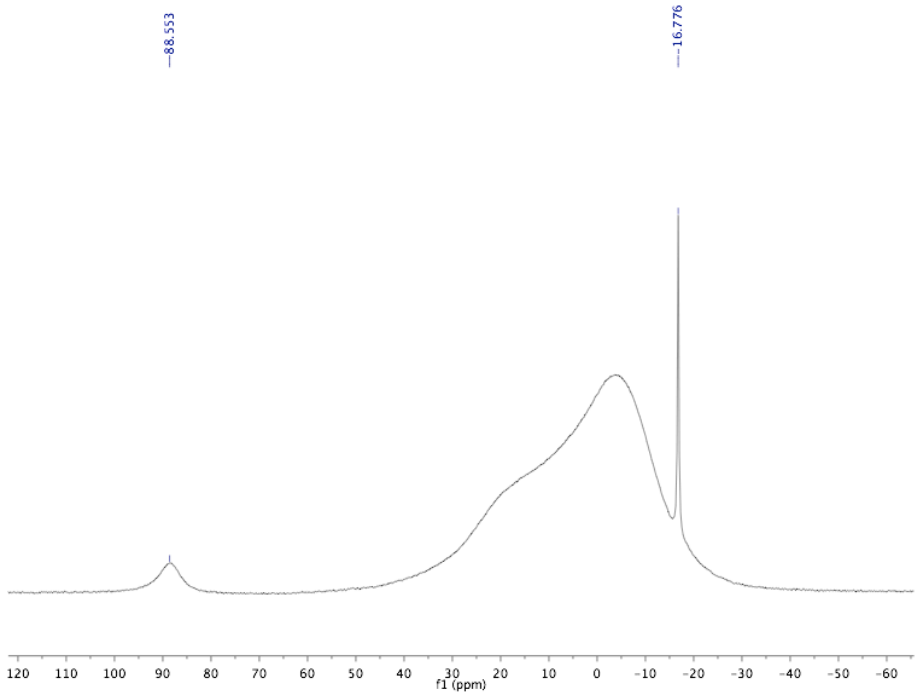


Figure S23. ^{11}B NMR.

Synthesis of *mer,trans*-$(Ph_2PCHCH_2)_2Mn(CO)_3Br$.

A 100 mL Teflon-stoppered pressure vessel was charged with 1.612 g (5.86 mmol) $Mn(CO)_5Br$, 2.49 g (11.7 mmol) diphenylvinylphosphine, 25 mL toluene, and a magnetic stirbar. The orange solution with some undissolved solids was sealed and heated to 120 °C, and the mixture darkened, with almost all of the solids dissolved. After 24 hours, the reaction mixture was allowed to cool to room temperature, during which time yellow powder precipitated and brown crystals grew, leaving an orange solution. The solids were collected on a frit, and washed with 10 mL toluene and 10 mL pentane, and then dried under vacuum. When the brown crystals were pulverized, they yielded yellow powder. Drying the powder afforded 2.48 g (66%) *mer,trans*-$(Ph_2PCHCH_2)_2Mn(CO)_3Br$. **^{1}H NMR** ($CD_2Cl_2$, 500 MHz): δ 5.18 (t, J = 17.6 Hz, 2H, $Ph_2PCHC\mathit{H}_2$), 6.01 (dd, J = 12.0, 35.2, 2H, $Ph_2PCHC\mathit{H}_2$), 7.24 (m, 2H, $Ph_2PC\mathit{H}CH_2$), 7.47 (br, 12H, 2H, Ph_2PCHCH_2), 7.68 (br, 8H, Ph_2PCHCH_2). **^{31}P{^{1}H} NMR** (THF-d_8, 121 MHz): δ 49.0. **^{13}C{^{1}H} NMR** (CD_2Cl_2, 126 MHz): δ 128.77 (t, J_{PC} = 4.7 Hz), 130.03, 130.72, 133.87 (t, J_{PC} = 4.8 Hz), 134.01 (m), 135.23 (m), 217.21 (br m, *trans*-CO), 223.39 (CO). **IR** (CH_2Cl_2): ν_{CO} 2039 (w), 1954 (s), 1912 (m) cm^{-1}. **HRMS** (FAB$^+$): m/z calcd for $C_{31}H_{26}BrMnO_3P_2$: 641.9921. Found: 641.9866.

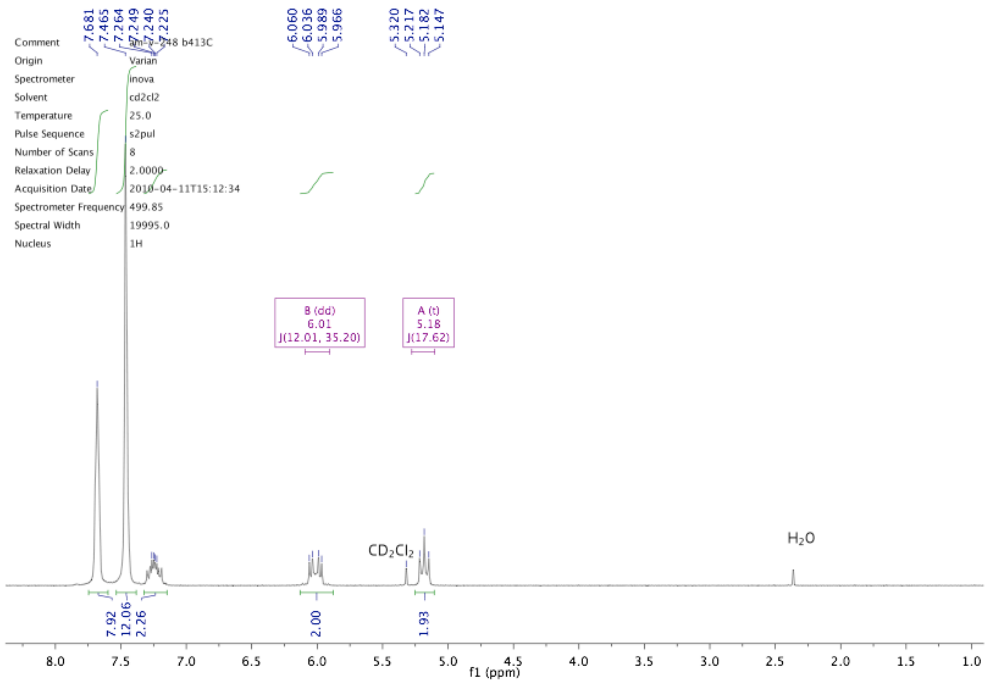


Figure S24. ^{1}H NMR.

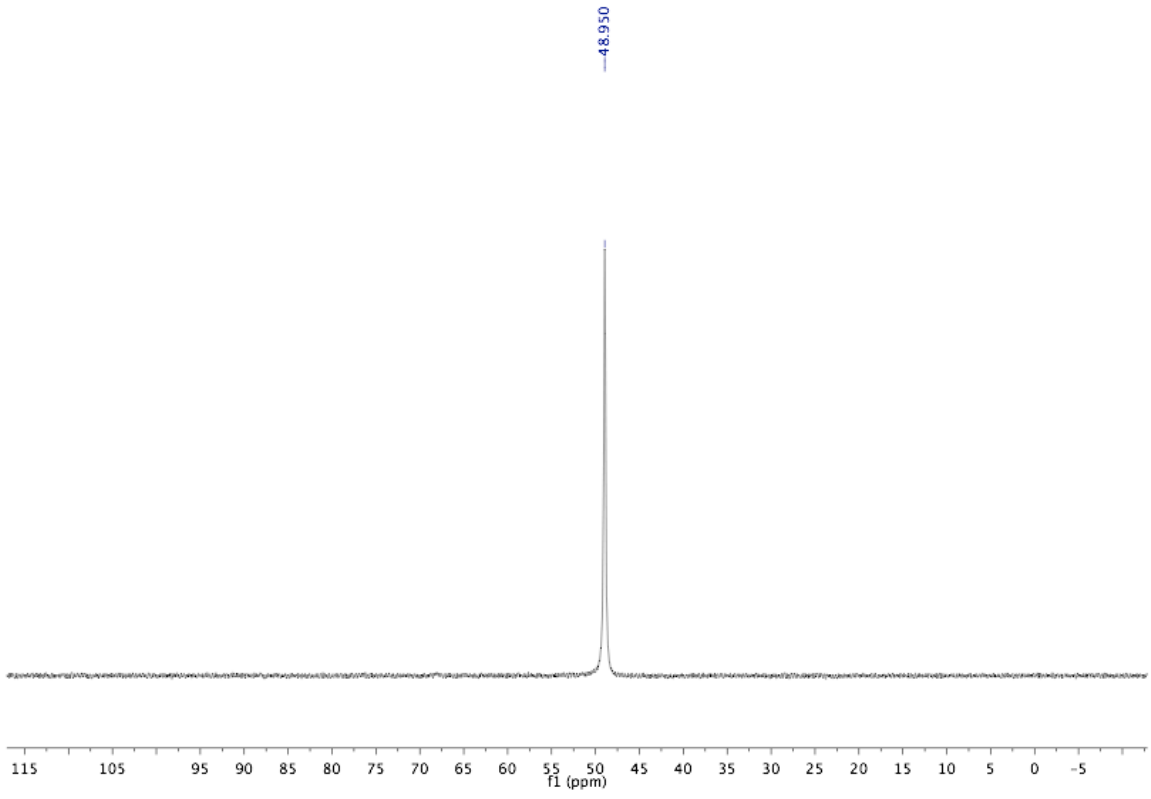


Figure S25. $^{31}P\{^{1}H\}$ NMR.

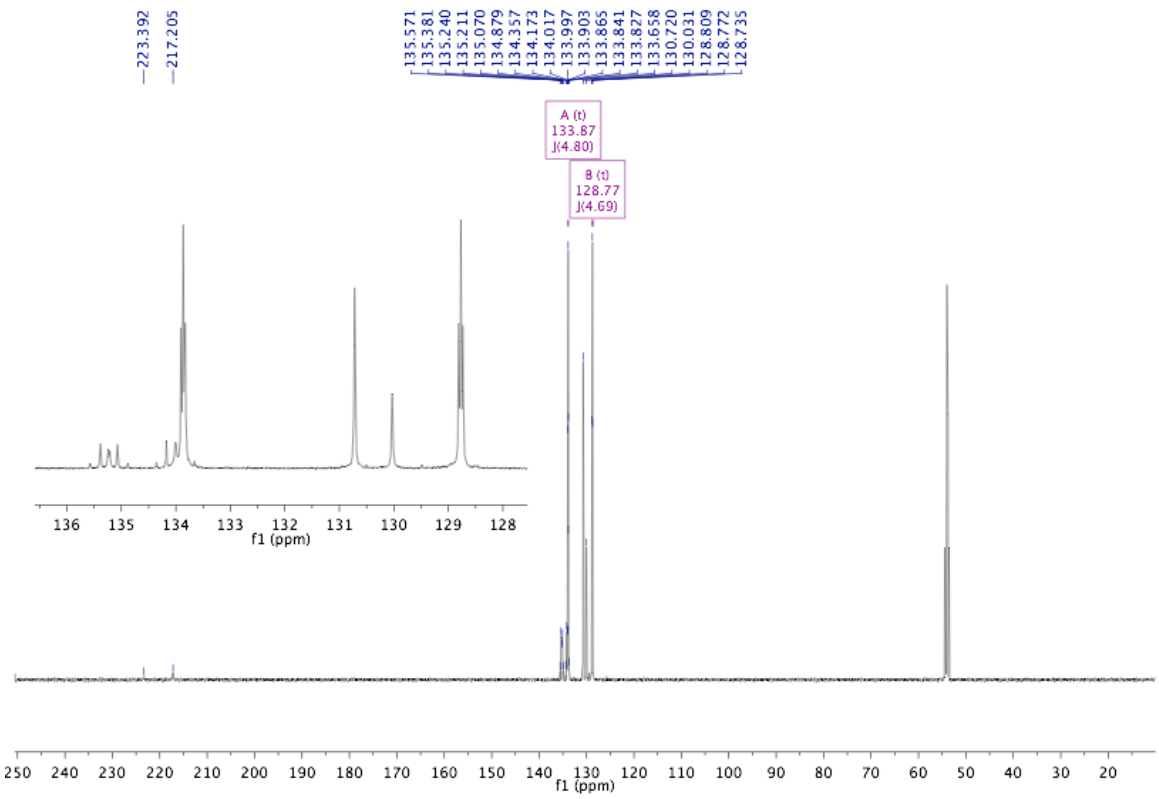


Figure S26. $^{13}C\{^{1}H\}$ NMR.

Synthesis of *trans*-[$(Ph_2PCHCH_2)_2Mn(CO)_4$][BF_4].

A 100 mL Teflon-stoppered pressure vessel was charged with 1.515 g (2.35 mmol) *mer,trans*-$(Ph_2PCHCH_2)_2Mn(CO)_3Br$, 0.596 g (3.06 mmol) $AgBF_4$, and a stirbar. 40 mL of CH_2Cl_2 was added, and the vessel was sealed and protected from light. The reaction mixture was boil-degassed, and 1 atm CO was introduced to the vessel. The dark orange turbid mixture was stirred for 20 hours, at which point it was boil-degassed to remove excess CO, and filtered through celite, affording a bright yellow solution. The filtrate was dried *in vacuo*, affording 1.6 g (100%) of yellow product. **^{1}H NMR** (CD_2Cl_2, 500 MHz): δ 5.40 (t, J = 18.8 Hz, 2H, Ph_2PCHCH_2), 6.30 (dd, J = 10.9, 40.5 Hz Ph_2PCHCH_2), 7.02 (m, 2H, Ph_2PCHCH_2), 7.55-7.65 (m, 20H, Ph_2PCHCH_2). **^{31}P{^{1}H} NMR** (CD_2Cl_2, 121 MHz): δ 44.2. **^{13}C{^{1}H} NMR** (CD_2Cl_2, 126 MHz): δ

130.29 (dd, J_{PC} = 2.1, 51.8 Hz), 130.32 (m, *o*-Ph_2PCHCH_2), 131.33 (dd, J_{PC} = 2.2, 46.8 Hz), 132.87 (m, *m*-Ph_2PCHCH_2), 132.91, 134.12, 211.3 (br, CO). **IR** (CH_2Cl_2): ν_{CO} 2003 cm^{-1}. **HRMS (FAB$^+$)**: m/z cald for $[C_{32}H_{26}MnO_4P_2]^+$: 591.0687. Found: 591.0672, 563.0756 (-CO).

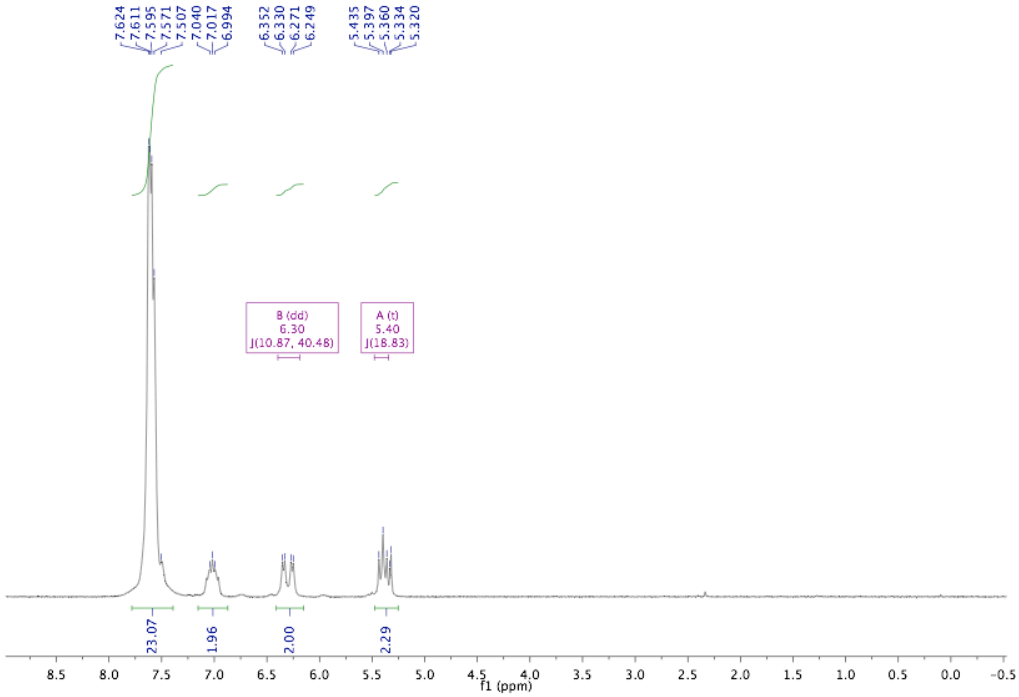


Figure S27. ^1H NMR.

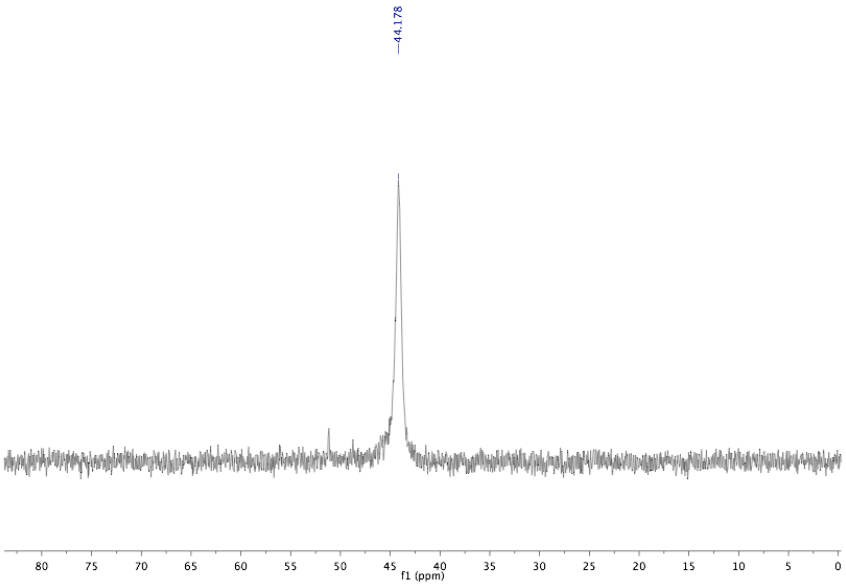


Figure S28. $^{31}P\{^1H\}$ NMR.

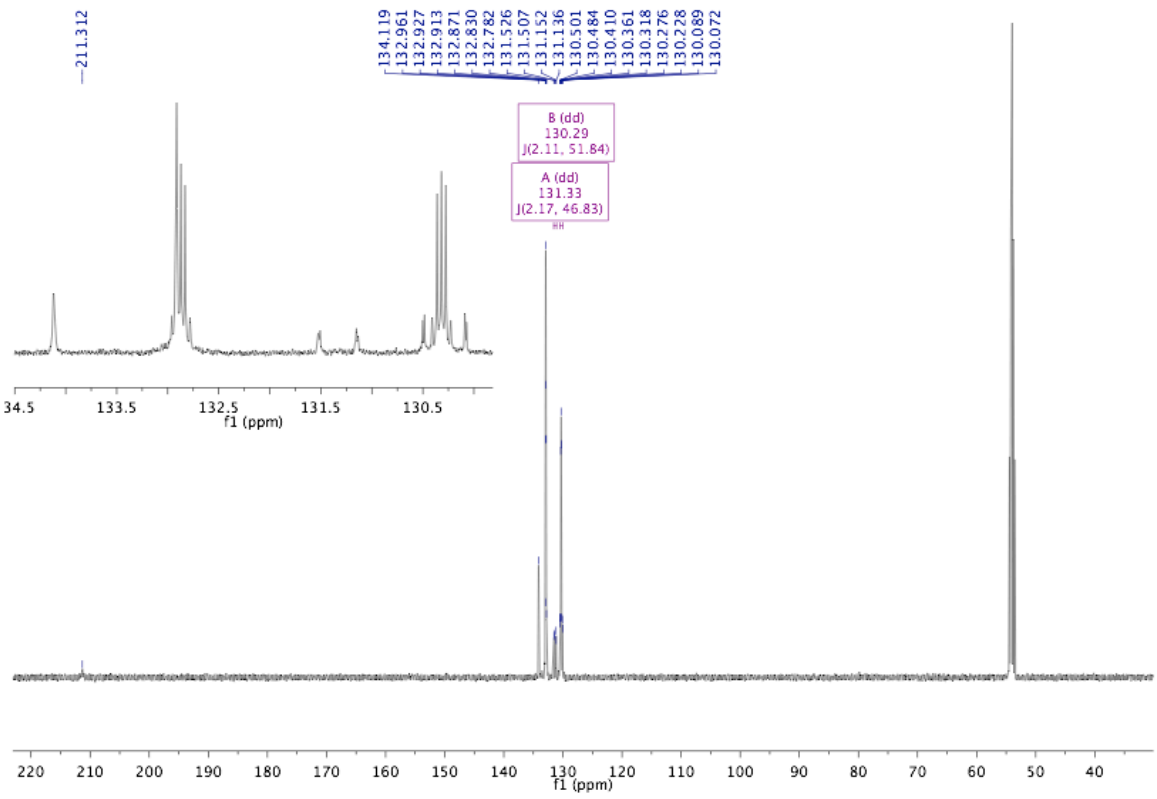


Figure S29. $^{13}C\{^{1}H\}$ NMR.

Synthesis of *trans*-[$(Ph_2P(CH_2)_2B(C_8H_{14}))_2Mn(CO)_4$][$BF_4$] ([1-$E_2$-Mn][$BF_4$]).

A 20 mL scintillation vial was charged with 641 mg (0.945 mmol) *trans*-[$(Ph_2PCHCH_2)_2Mn(CO)_4$][BF_4], and 20 mL CH_2Cl_2 was added. If any residual silver salts were present, as black insoluble solids, the solution was filtered. The solution was added to a 100 mL Teflon-stoppered pressure vessel, to which was then added 692 mg (5.67 mmol) 9-BBN and a stirbar. The yellow solution turned dark orange quickly. The reaction vessel was sealed and moved to a 60 ˚C oil bath, where it was heated with stirring for 10 days. At this time the reaction was allowed to cool to room temperature, and the mixture was filtered through celite, giving a bright yellow solution. The filtrate was concentrated to 3 mL, and 15 mL pentane was added,

producing an orange oil with yellow solution above it. The solvent was decanted from the oil, and the oil was washed with 3 x 5 mL pentane, and then dried under vacuum, giving 700 mg (80%) crude [**1-E$_2$-Mn**][BF$_4$], ~90% pure by NMR spectroscopy. Further purification was achieved by dissolving the solids in 7 mL toluene, and letting the solution stand overnight, which yielded analytically pure yellow polycrystalline [**1-E$_2$-Mn**][BF$_4$] (460 mg, 53%). **^{1}H NMR** (THF-d_8, 300 MHz): δ 0.54 (m, 4H), 0.70 (4H), 1.23 (m, 4H), 1.48 (16H), 1.68 (m, 4H), 2.74 (m, 4H), 7.52 (m, 12H), 7.71 (m, 8H). **^{31}P{^{1}H} NMR** (THF-d_8, 121 MHz): δ 51.5. **^{13}C{^{1}H} NMR** (CD_2Cl_2, 126 MHz): δ 20.83 (br, $Ph_2PCH_2\mathit{C}H_2B(C_8H_{14})$), 23.51 ($Ph_2P\mathit{C}H_2CH_2B(\mathit{C}_8H_{14})$), 28.14 (dd, J_{PC} = 2.8, 28.6 Hz, $Ph_2P\mathit{C}H_2CH_2B(C_8H_{14})$), 31.91 (br, $Ph_2PCH_2CH_2B(\mathit{C}_8H_{14})$), 33.71 ($Ph_2PCH_2CH_2B(\mathit{C}_8H_{14})$), 130.30 (m, *m*-Ph), 131.91 (dd, J_{PC} 1.7, 47.6 Hz, *ipso*-Ph), 132.25 (m, *o*-Ph), 132.54 (*p*-Ph), 212.18 (br, CO). **^{11}B NMR** (CD_2Cl_2, 160 MHz): δ -1.2 ($\mathit{B}F_4$), 86.9 (br, -$\mathit{B}(C_8H_{14})$). **^{19}F NMR** (CD_2Cl_2, 282 MHz): δ -152.5 (br). **IR** (THF): ν_{CO} 1995 cm^{-1}.

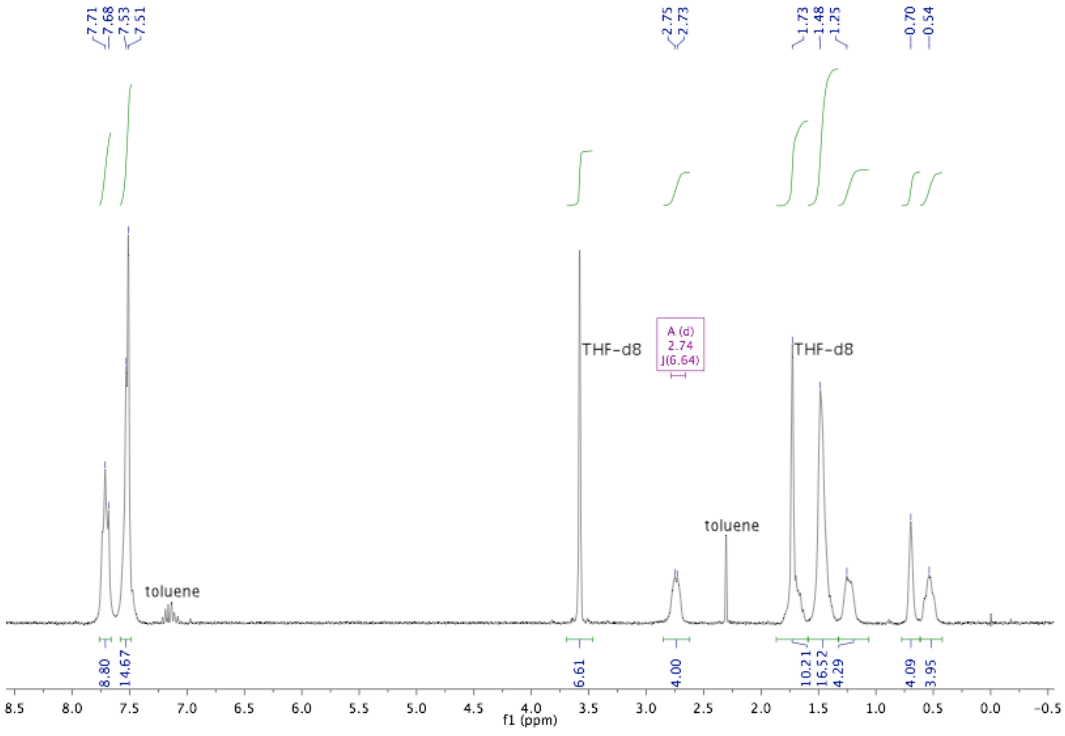


Figure S30. ^{1}H NMR.

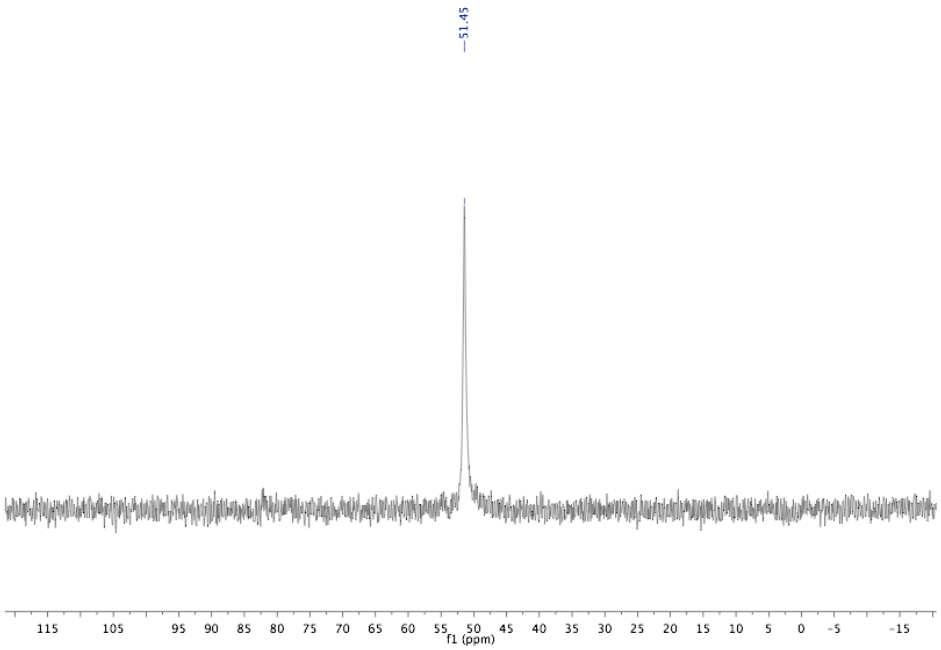


Figure S31. $^{31}P\{^{1}H\}$ NMR.

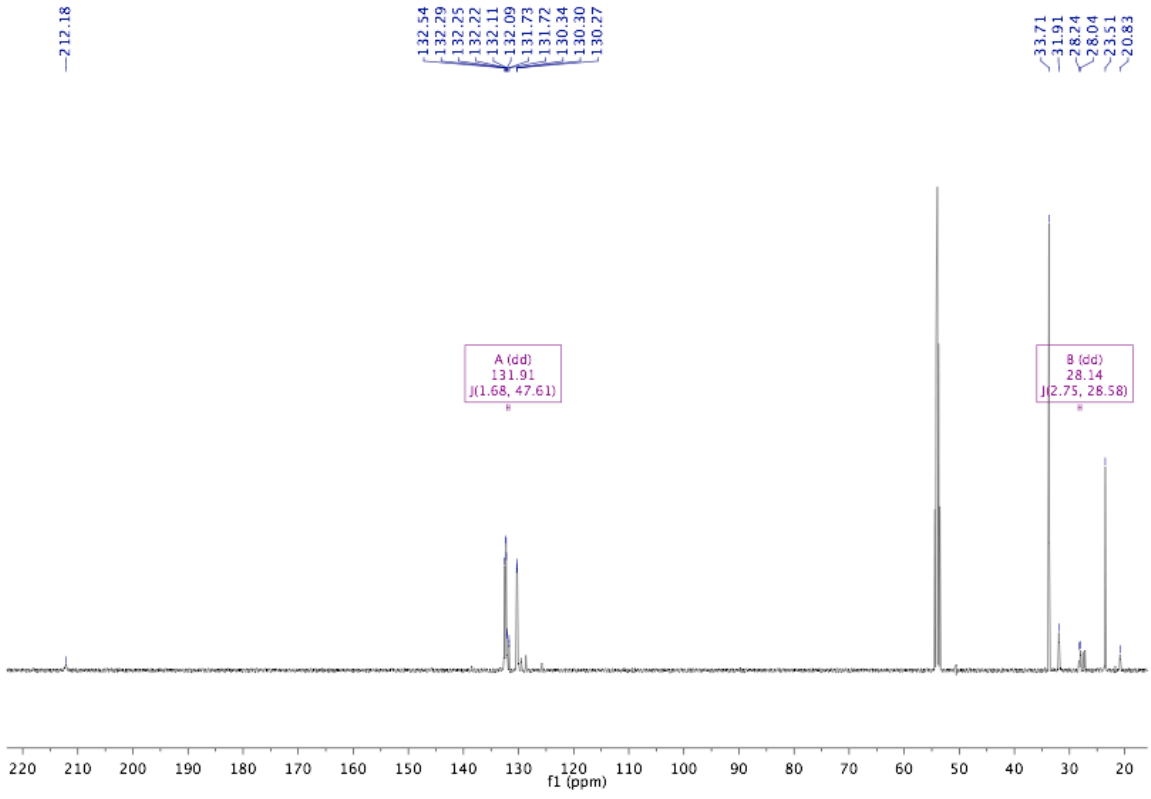


Figure S32. $^{13}C\{^{1}H\}$ NMR.

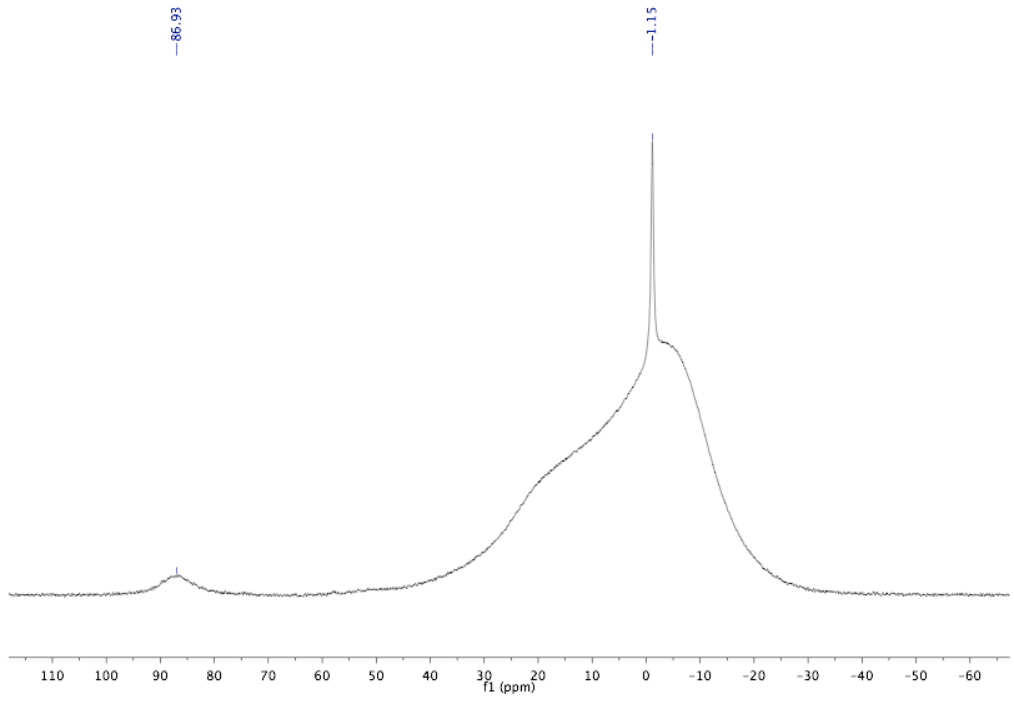


Figure S33. ^{11}B NMR.

Synthesis of *mer,trans*-$(Ph_2PCH_2CHCH_2)_2Re(CO)_3Br$.

A 60 mL Teflon-stoppered pressure tube was charged with 741 mg (1.82 mmol) $Re(CO)_5Br$, 825 mg (3.64 mmol, 2 equiv) $Ph_2PCH_2CHCH_2$, 15 mL toluene, and a stirbar. The tube was sealed, removed from the glovebox, and heated to 120 °C. After 5 days, the reaction was cooled to ambient temperature, degassed to remove liberated CO, and brought into a glovebox. All solvents were removed under vacuum, the solids were washed with 25 mL pentane, and collected on a frit. The white powder was dried, giving 1.28 g (1.59 mmol, 88%) pure *mer,trans*-$(Ph_2PCH_2CHCH_2)_2Re(CO)_3Br$. **^{1}H NMR** ($CD_2Cl_2$, 300 MHz): δ 3.62 (m, 4H, $Ph_2PCH_2CHCH_2$), 4.85 (dd, $^4J_{PH}$=1.8 Hz, J_{HH}=17.3 Hz, 2H, $Ph_2PCH_2CHCH_2$), 4.98 (dd, $^4J_{PH}$=1.7 Hz, J_{HH}=10.3 Hz, 2H, $Ph_2PCH_2CHCH_2$), 5.63 (m, 2H, $Ph_2PCH_2CHCH_2$), 7.40-7.48 (m, 12H, $Ph_2PCH_2CHCH_2$), 7.56-7.65 (m, 8H, $Ph_2PCH_2CHCH_2$). **^{31}P{^{1}H} NMR** (CD_2Cl_2, 121 MHz): δ -0.9 (s). **^{13}C{^{1}H}**

NMR (CD_2Cl_2, 125 MHz): δ 35.88 (t, $^1J_{PC}$ = 14.4 Hz, $Ph_2PCH_2CHCH_2$), 120.53 (t, $^3J_{PC}$ = 5.4 Hz, $Ph_2PCH_2CHCH_2$), 128.76 (t, J_{PC} = 4.7 Hz, *m*-$Ph_2PCH_2CHCH_2$), 130.58 (t, $^2J_{PC}$ = 2.6 Hz, $Ph_2PCH_2CHCH_2$), 130.68 (br t, J_{PC} < 1 Hz, *p*-$Ph_2PCH_2CHCH_2$), 133.36 (t, J_{PC} = 5.0 Hz, *o*-$Ph_2PCH_2CHCH_2$), 135.21 (t, $^1J_{PC}$ = 23.3 Hz, *ipso*-$Ph_2PCH_2CHCH_2$), 190.38 (t, $^2J_{PC}$ = 6.7 Hz, *C*O *trans* to Br), 192.25 (t, $^2J_{PC}$ = 8.5 Hz, *C*O). **IR (CD_2Cl_2):** υ_{CO}, 2060, 1958, 1899 cm^{-1}. Anal. Calcd. for $C_{33}H_{30}BrO_3P_2Re$: C, 49.38; H, 3.77. Found: C, 49.32; H, 3.38.

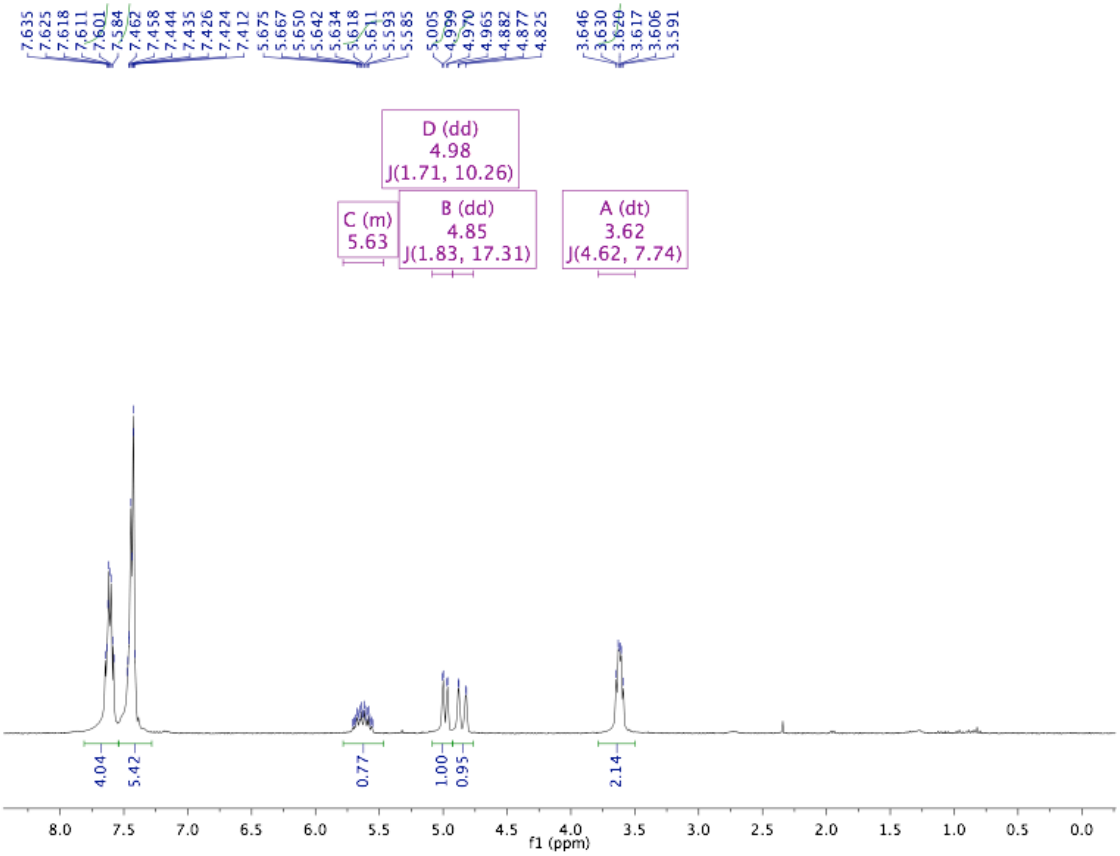


Figure S34. ^{1}H NMR.

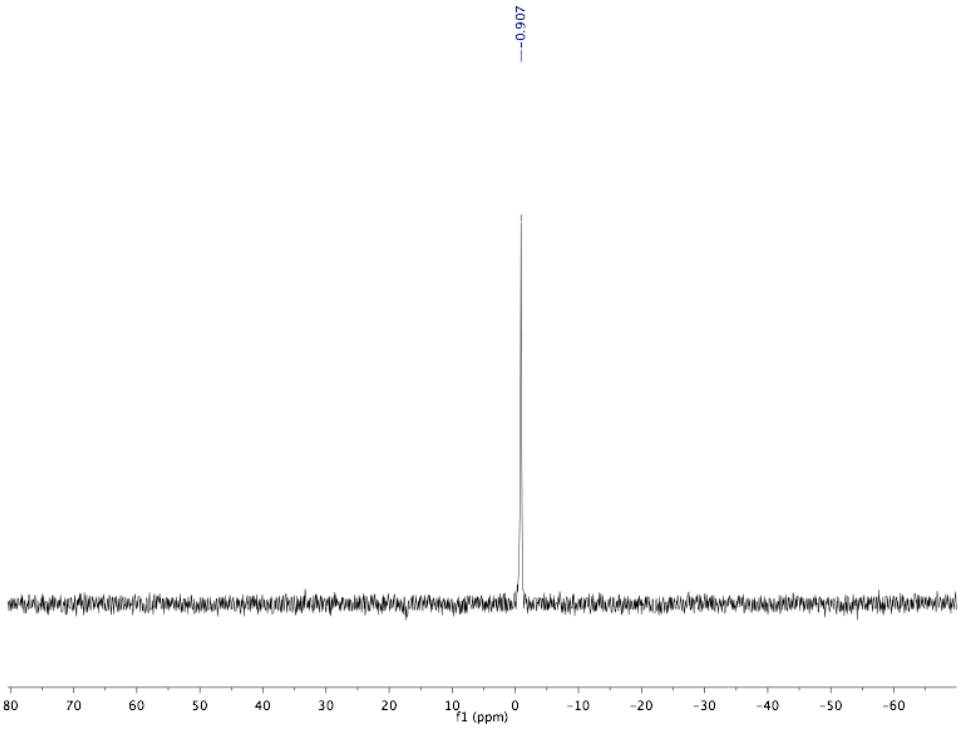


Figure S35. $^{31}P\{^{1}H\}$ NMR.

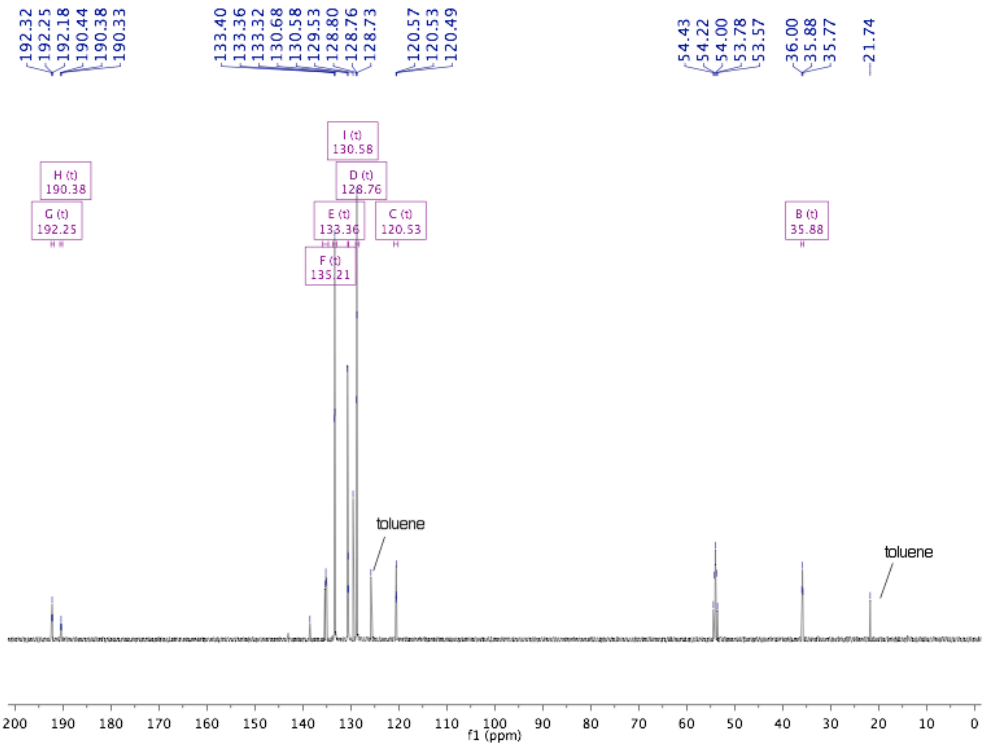


Figure S36. $^{13}C\{^{1}H\}$ NMR (with residual toluene).

Synthesis of *trans*-[$(Ph_2PCH_2CHCH_2)_2Re(CO)_4$][$BF_4$].

An 80 mL Teflon-stoppered pressure vessel was charged with 1.2 g (1.49 mmol) *mer,trans*-$(Ph_2PCH_2CHCH_2)_2Re(CO)_3Br$, 0.378 g (1.94 mmol, 1.3 equiv) $AgBF_4$, 20 mL CH_2Cl_2, and a stirbar. The mixture started to become cloudy. The vessel was quickly sealed and removed from the glovebox, whereupon it was frozen in liquid nitrogen. Two freeze-pump-thaw sequences were followed by addition of 1 atm CO. The vessel was sealed (at room temperature), protected from light, and stirred overnight (8-12 hours). The reaction mixture was then boil-degassed on a Schlenk line, and brought into a glovebox. The mixture was filtered through celite and dried, giving 0.832 g (0.99 mmol, 67%) of off-white solids, of ~95% purity (^{31}P NMR). This crude material was crystallized from CH_2Cl_2/pentane to afford 0.55 g (0.657 mmol, 44%) white *trans*-[$(Ph_2PCH_2CHCH_2)_2Re(CO)_4$][$BF_4$]. **^{1}H NMR** ($CD_2Cl_2$, 300 MHz): δ 3.56-3.66 (m, 4H), 5.12-5.32 (m, 4H), 5.34-5.49 (m, 4H), 7.44-7.62 (m, 20H). **^{31}P{^{1}H} NMR** (CD_2Cl_2, 121 MHz): δ -5.7. **^{13}C{^{1}H} NMR** (CD_2Cl_2, 151 MHz). δ 38.99 (t, $^1J_{PC}$ = 16.0, $Ph_2PCH_2CHCH_2$), 123.89 (t, $^3J_{PC}$ = 6.1 Hz, $Ph_2PCH_2CHCH_2$), 127.97 (t, $^2J_{PC}$ = 2.6 Hz, $Ph_2PCH_2CHCH_2$), 130.15 (t, J_{PC} = 5.2 Hz, *m*-$Ph_2PCH_2CHCH_2$), 132.39 (t, J_{PC} = 5.2 Hz, *o*-$Ph_2PCH_2CHCH_2$), 132.63 (br t, J < 2 Hz, *p*-$Ph_2PCH_2CHCH_2$), 132.6 (t, J_{PC} = 25.2 Hz, *ipso*-$Ph_2PCH_2CHCH_2$), 185.22 (t, $^2J_{PC}$ = 7.5 Hz, Re-*C*O)**.** **^{19}F NMR** (CD_2Cl_2): δ -152.5. IR (CD_2Cl_2): υ_{CO}, 2004 cm^{-1}. **HRMS** (TOF ES$^+$): m/z calcd. for $C_{34}H_{30}O_4P_2Re$: 751.1179. Found: 751.1177 (M^+).

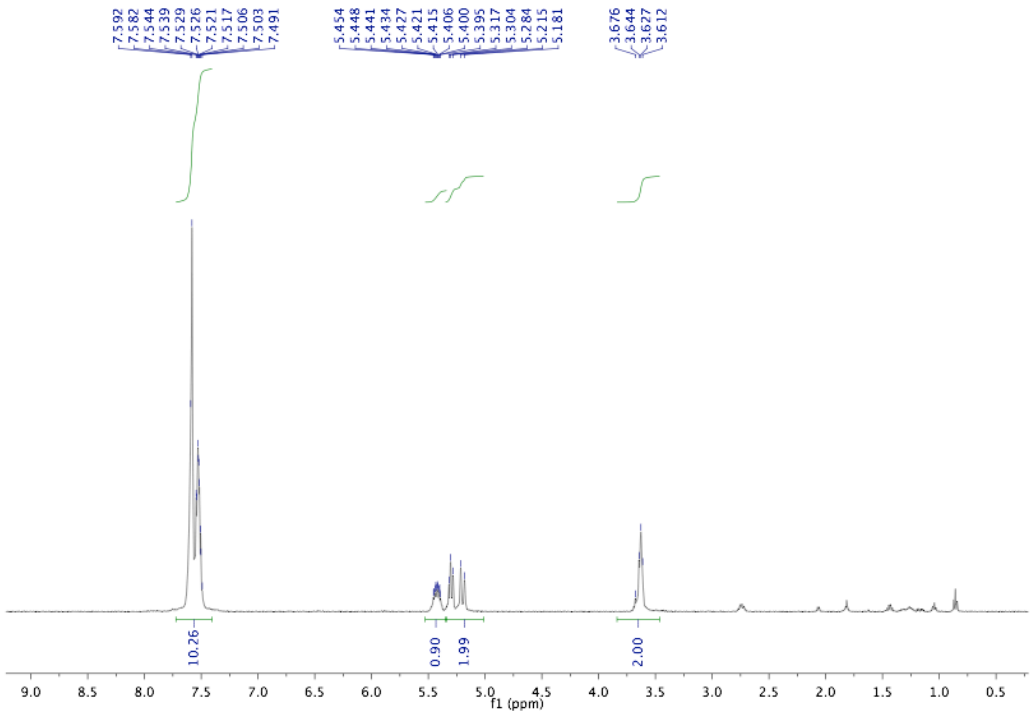


Figure S37. ^{1}H NMR.

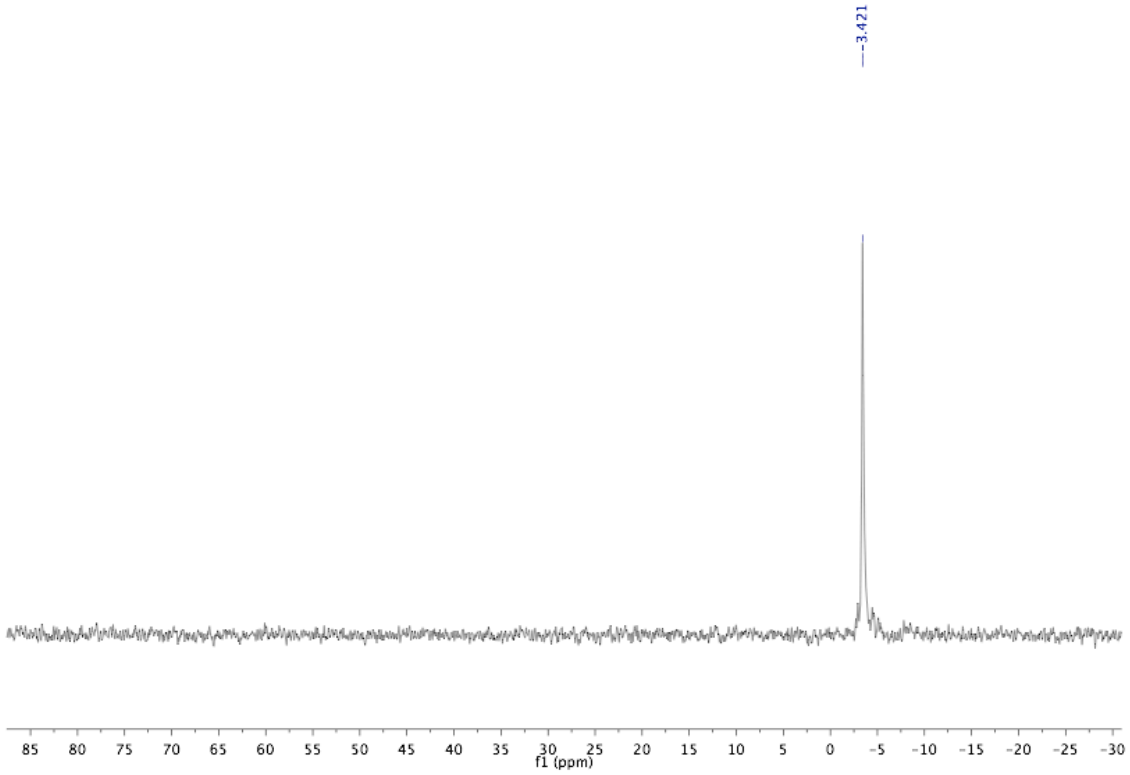


Figure S38. $^{31}P\{^{1}H\}$ NMR.

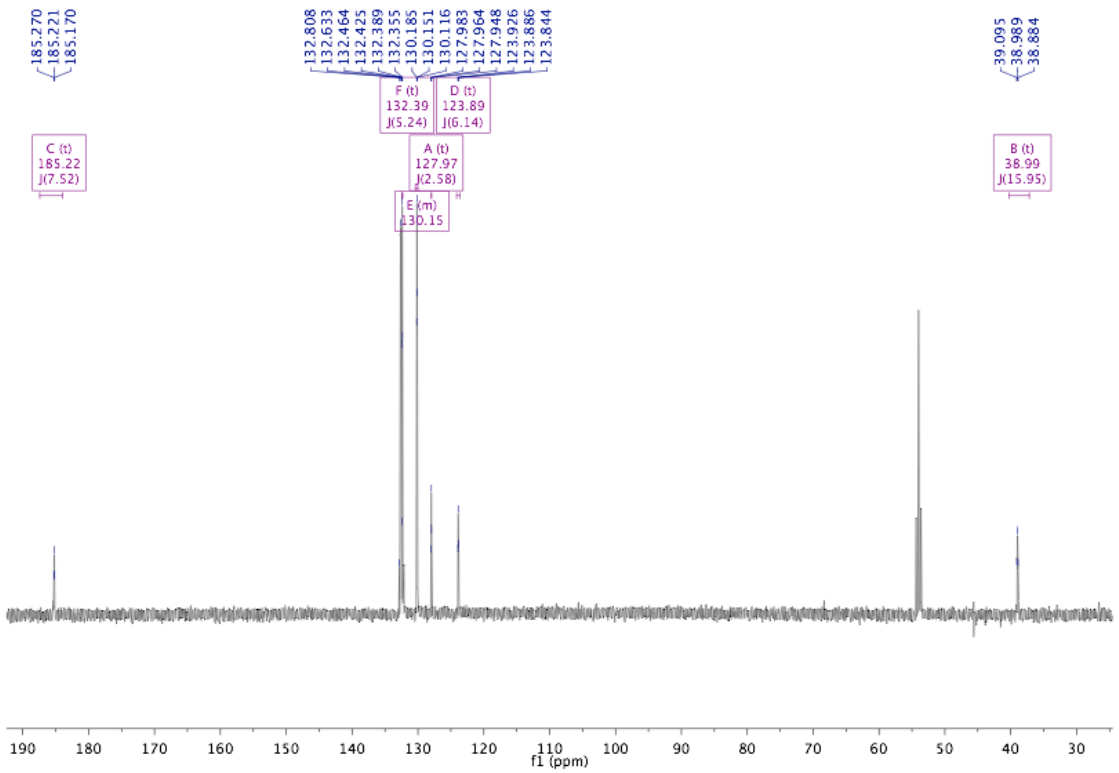


Figure S39. $^{13}C\{^{1}H\}$ NMR (with residual toluene).

Synthesis of *trans*-[$(Ph_2P(CH_2)_3B(C_8H_{14}))_2Re(CO)_4$][$BF_4$] ([1-$P_2$][$BF_4$]).

A 60 mL Teflon-stoppered pressure vessel was charged with 239 mg (0.285 mmol) *trans*-[$(Ph_2PCH_2CHCH_2)_2Re(CO)_4$][$BF_4$], 69.6 mg (0.576 mmol) 9-BBN, and 15 mL CH_2Cl_2. A stirbar was added, and the vessel was sealed and the reaction vessel was heated to 60 °C. After 8 hours, the reaction mixture was cooled, and returned to the glovebox. After filtration, the solvent was removed to give 301 mg (0.278 mmol, 97%) crude white [**1-P_2**][BF_4]. The purity of this material was >95% (assessed by ^{1}H and ^{31}P NMR), and was used without further purification. If protic impurities appear to be present, [**1-P_2**][BF_4] can be treated with TMSCl (10 equiv. in CH_2Cl_2). After stirring for one hour, the mixture was filtered, the solvents removed, and the white solids

washed with pentane. Crystallization from THF/pentane layer (-35 °C) afforded spectroscopically pure material. **^{1}H NMR** (CD_2Cl_2, 500 MHz): δ 1.15 (m, 4H), 1.46 (br, 4H), 1.5-1.6 (m, 16H), 1.75-1.85 (m, 12H), 2.76 (br, 4H), 7.50-7.54 (m, 8H), 7.58 (m, 12H). **^{31}P{^{1}H} NMR** (CD_2Cl_2, 202 MHz): δ -4.3. **^{11}B{^{1}H} NMR** (CD_2Cl_2, 160 MHz): -0.5 (BF_4), 88.5 ($Ph_2P(CH_2)_3B(C_8H_{14})$). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 126 MHz): δ 20.31, 23.64, 29.0 (br), 31.5 (br), 33.61, 36.28 (t, J_{PC} = 15.5 Hz), 130.1 (t, J_{PC} = 5.2 Hz), 132.2 (t, J_{PC} = 5.2 Hz), 132.16 (t, J_{PC} = 5.4 Hz), 132.43, 132.85 (dd, J_{PC} = 25.7, 26.5 Hz), 185.58 (t, J_{PC} = 7.4 Hz). **IR** (CH_2Cl_2): υ_{CO}, 1999 cm^{-1}. **HRMS** (TOF HR-ESI^{+}): Calcd for $C_{50}H_{60}B_2O_4P_2Re$: 995.3802. Found: 995.3804.

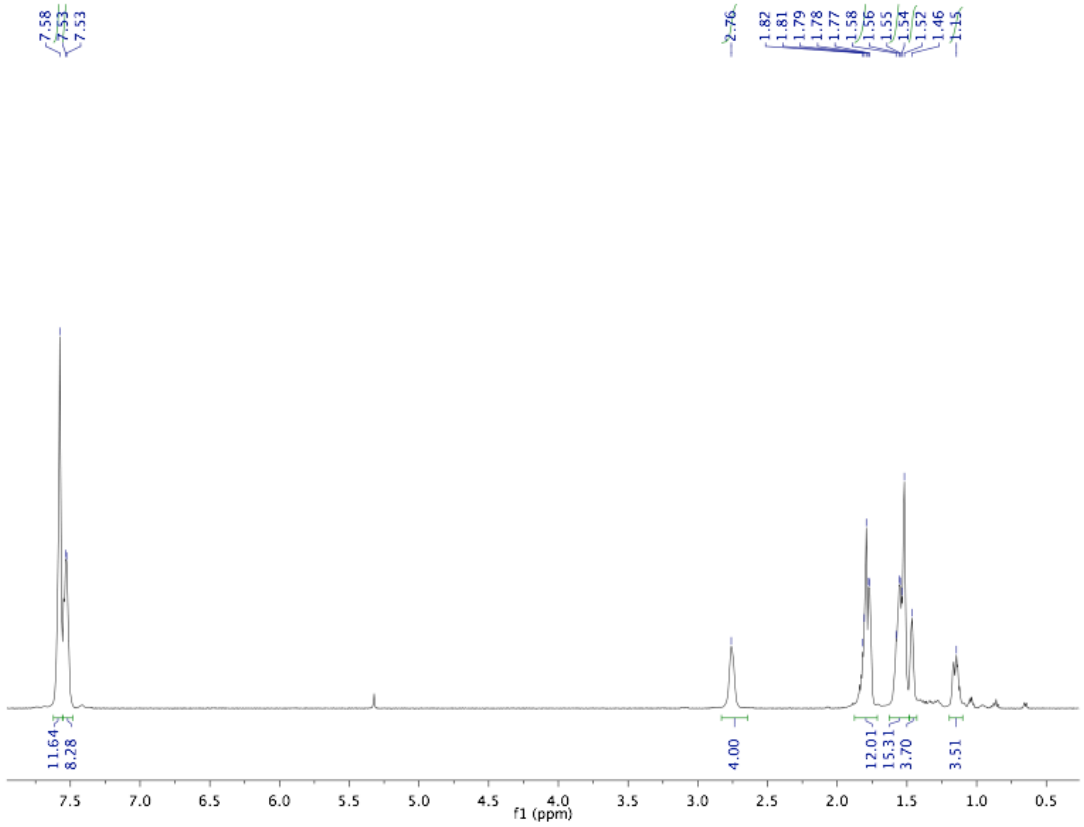


Figure S40. ^{1}H NMR.

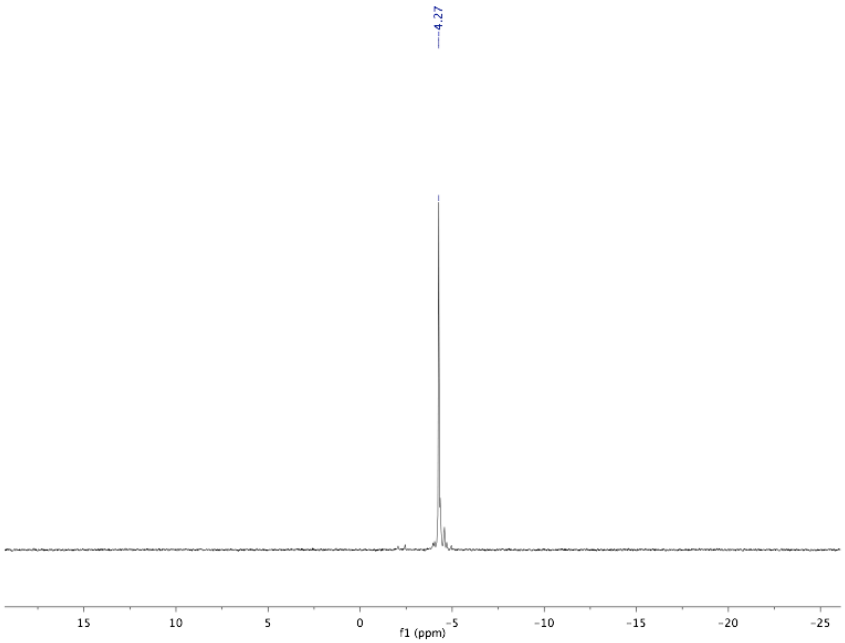


Figure S41. $^{31}P\{^{1}H\}$ NMR.

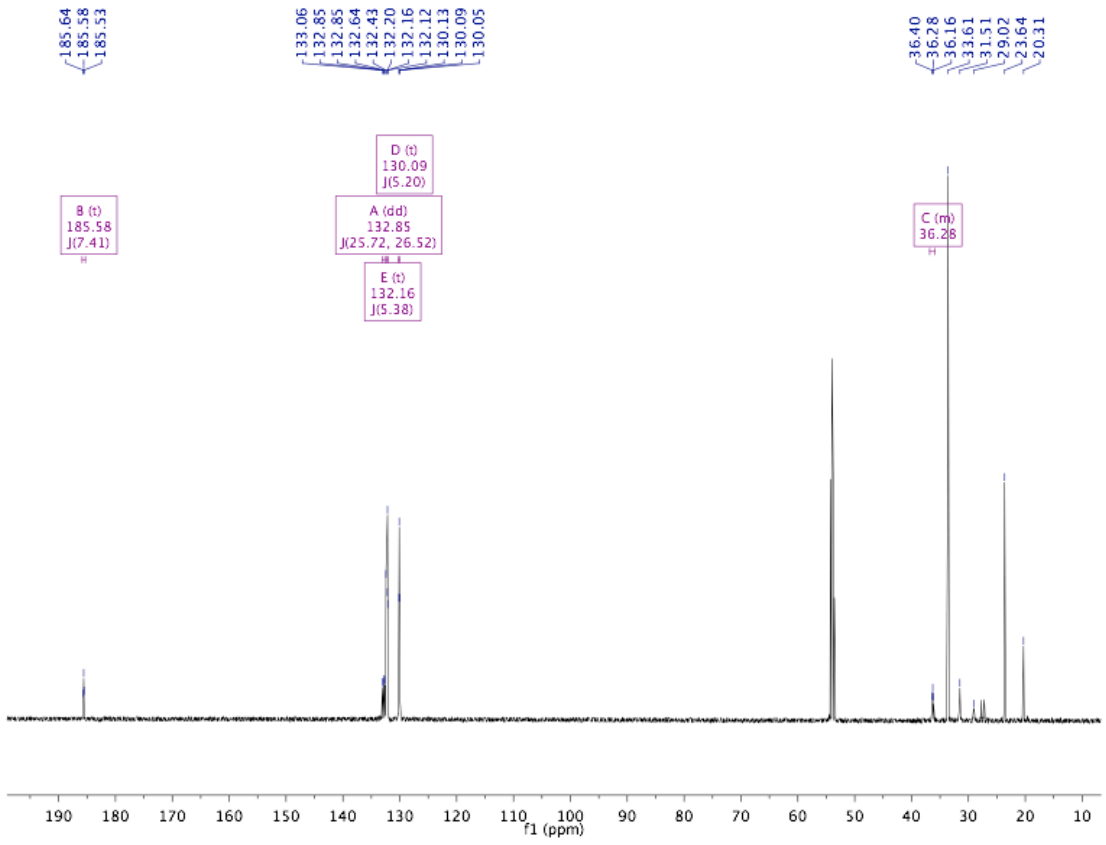


Figure S42. $^{13}C\{^{1}H\}$ NMR.

Synthesis of [($Ph_2PCH_2B(C_8H_{14})$)$Re(CO)_5$][OTf] ([1-M_1][OTf]).

Either isolated or in situ generated $Re(CO)_5OTf$ could be used in this synthesis. A representative experiment did not isolate $Re(CO)_5OTf$, which was formed by adding 800 mg (3.1 mmol, 1.25 equiv) solid AgOTf to a 30 mL stirring solution of 1.01 g (2.50 mmol) $Re(CO)_5Br$ in CH_2Cl_2. The mixture was protected from light and allowed to stir for 6 hours, over which time a large amount of precipitates formed. The mixture was filtered into a 100 mL Teflon-stoppered glass pressure vessel charged with 800 mg (2.50 mmol, 1 equiv) $Ph_2PCH_2B(C_8H_{14})$. The vessel was sealed after addition of a stirbar and removed from the glovebox and heated to 60 °C. After 5 days heating, the reaction was allowed to cool to ambient temperature, returned to the glovebox, where it was filtered, and the solvent removed from the clear colorless filtrate under vacuum to give white solid [**1-M_1**][OTf] in 93% purity. The material was washed with 5x15 mL Et_2O, and dried in vacuo to give analytically pure [**1-M_1**][OTf] (1.45 g, 74%). **^{1}H NMR** (CD_2Cl_2, 300 MHz): δ 0.92-1.01 (m, 2H), 1.37-1.44 (m, 6H), 1.65-1.75 (m, 6H), 3.37 (d, 11.7 Hz, 2H, $Ph_2PCH_2B(C_8H_{14})$), 7.58-7.65 (m, 10H, $Ph_2PCH_2B(C_8H_{14})$). **^{31}P{^{1}H} NMR** (CD_2Cl_2, 121 MHz): δ -14.7. **^{19}F NMR** (CD_2Cl_2, 282 MHz): δ -78.1. **^{13}C{^{1}H} NMR** (CD_2Cl_2, 125 MHz): δ 22.95, 29.66 (br d, J_{PC} = 24.3 Hz), 33.91, 35.11 (br), 121.61 (q, J_{FC} = 321 Hz, CF_3SO_3-), 130.37 (d, J_{PC} = 10.8 Hz), 131.91 (d, J_{PC} = 10.6 Hz), 132.89 (d, J_{PC} = 2.6 Hz), 133.08 (d, J_{PC} = 53.1 Hz), 175.9 (v. br d, axial *C*O), 179.3 (br, equatorial *C*O). **^{11}B{^{1}H} NMR** (CD_2Cl_2, 160 MHz): δ 88.3. **IR** (C_6D_5Cl): υ_{CO}, 2156 (w), 2099 (w), 2041 (vs) cm^{-1}. **Anal. Calcd.** for $C_{27}H_{26}BF_3O_8PReS$: C, 40.76; H, 3.29. Found: C, 40.49; H, 3.16.

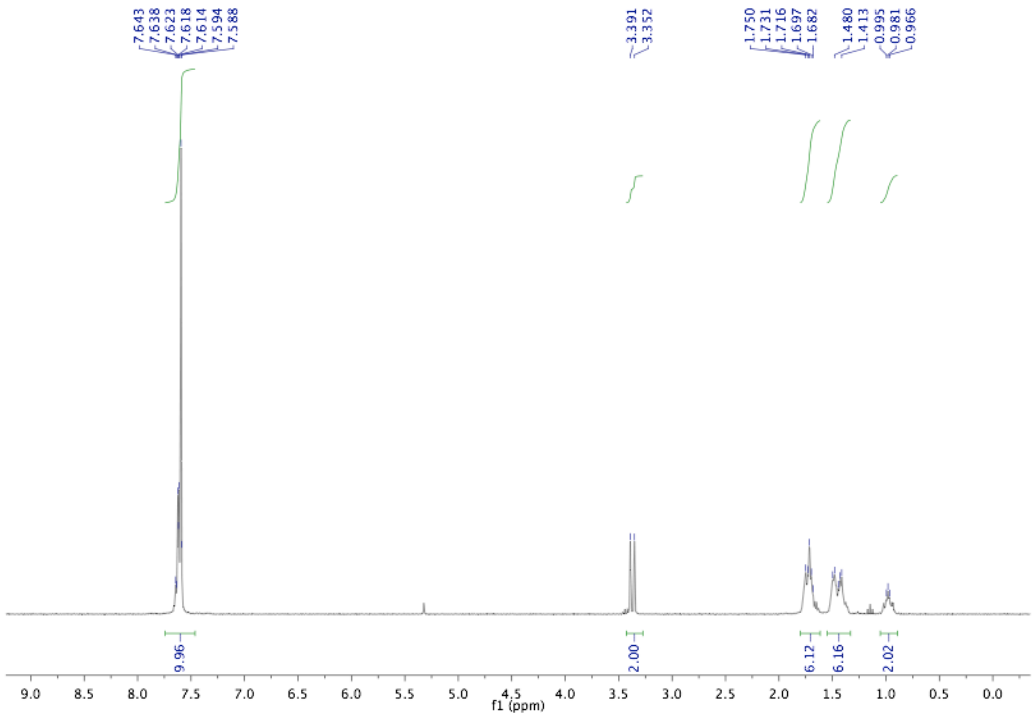


Figure S43. ^{1}H NMR.

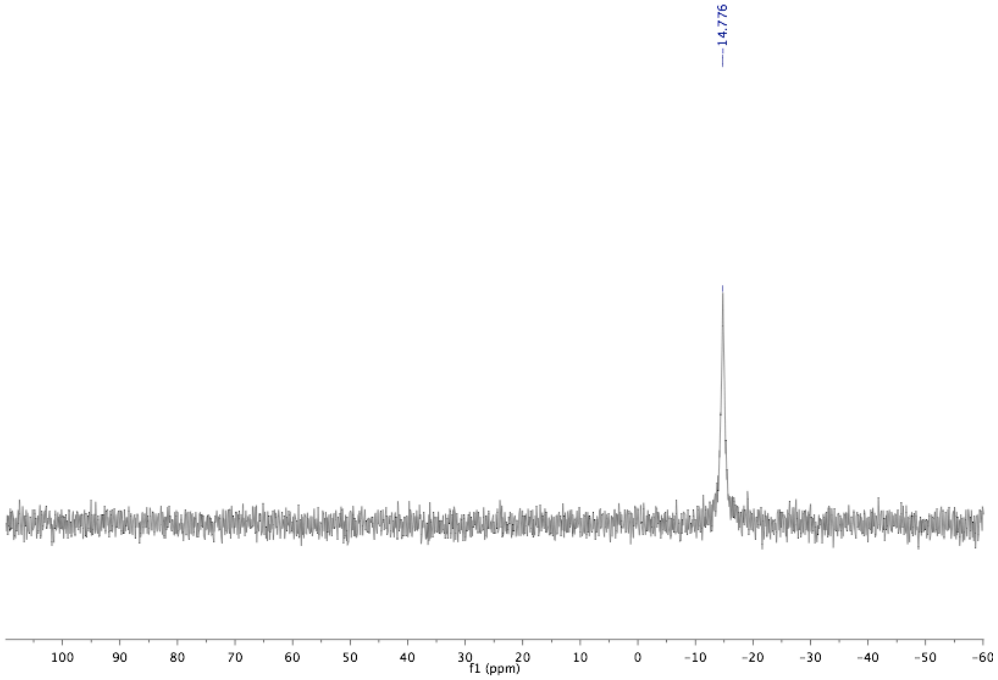


Figure S44. $^{31}P\{^{1}H\}$ NMR.

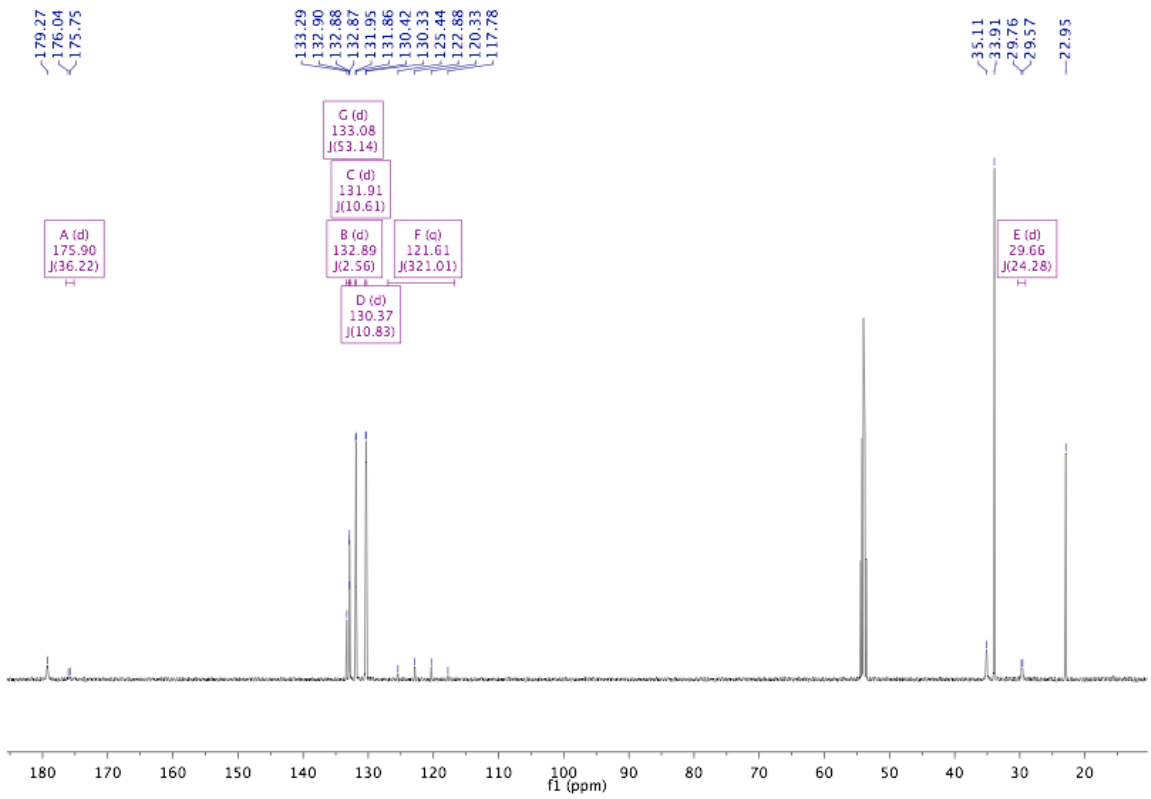


Figure S45. $^{13}C\{^{1}H\}$ NMR.

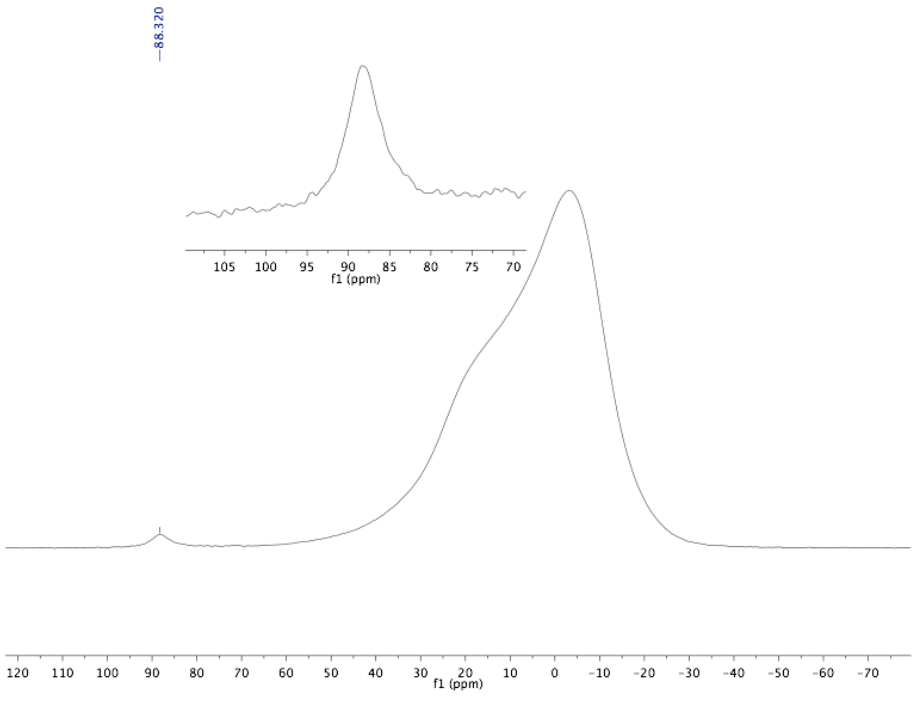


Figure S46. $^{11}B\{^{1}H\}$ NMR.

Synthesis of [($Ph_2P(CH_2)_2B(C_8H_{14})$)$Re(CO)_5$][OTf] ([1-$E_1$][OTf]).

A glass pressure vessel with a Teflon valve was charged with 0.402 g (0.844 mmol) $Re(CO)_5OTf$, 0.282 g (0.844 mmol) $Ph_2P(CH_2)_2B(C_8H_{14})$, 15 mL CH_2Cl_2 and a stirbar. The phosphinoborane did not fully dissolve. The flask was sealed and heated to 60 °C. After 15 minutes, all of the ligand had dissolved. After 48 hours, the reaction mixture was cooled to ambient temperature, at which point the vessel was pumped into the glovebox. The solution was filtered, and the solvents removed, giving a white powder: 0.670 g (0.827 mmol, 98% yield) of pure [**1-E_1**][OTf]. **^{1}H NMR** (CD_2Cl_2, 600 MHz): δ 1.15 (m, 2H), 1.34 (m, 2H), 1.57-1.63 (m, 4H), 1.69 (br, 2H), 1.78-1.88 (m, 6H), 2.99 (m, 2H), 7.54-7.58 (m, 4H), 7.62-7.64 (m, 6H)**. ^{31}P{^{1}H} NMR** (C_6D_5Cl, 121 MHz): δ 0.14 (s). **^{19}F NMR** (C_6D_5Cl, 282 MHz): δ -78.0. **^{11}B{^{1}H} NMR** (CD_2Cl_2, 160 MHz): δ 86.5 (br, s). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 126 MHz): δ 20.8 (br), 23.51, 27.5 (d, J_{PC} = 29.8), 32.0, 33.7, 121.6 (q, J_{FC} = 321 Hz, $CF_3SO_3^-$), 130.5 (d, J_{PC} = 10.6), 130.6 (d, J_{PC} = 52.6), 132.5 (d, J_{PC} = 9.9 Hz), 133.1 (d, J_{PC} = 2.5 Hz), 175.8 (br s, *C*O), 179.0 (br s, *C*O)**. IR (CD_2Cl_2):** υ_{CO}, 2156 (m), 2096 (w), 2064 (vs) cm^{-1}; υ_{SO}, 1274 cm^{-1}; υ_{CF}, 1161 cm^{-1}. **HRMS** (TOF ES^+): m/z calcd for $[C_{27}H_{28}BO_5PRe]^+$: 661.1331. Found: 661.1349.

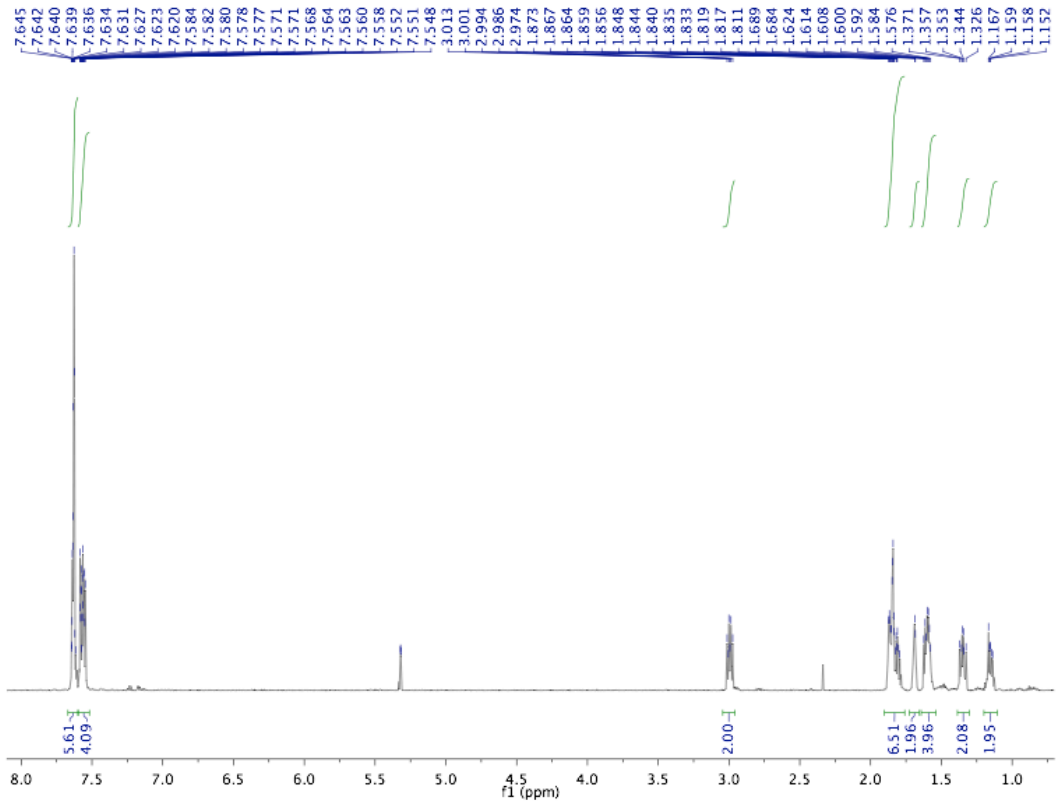


Figure S47. ^{1}H NMR.

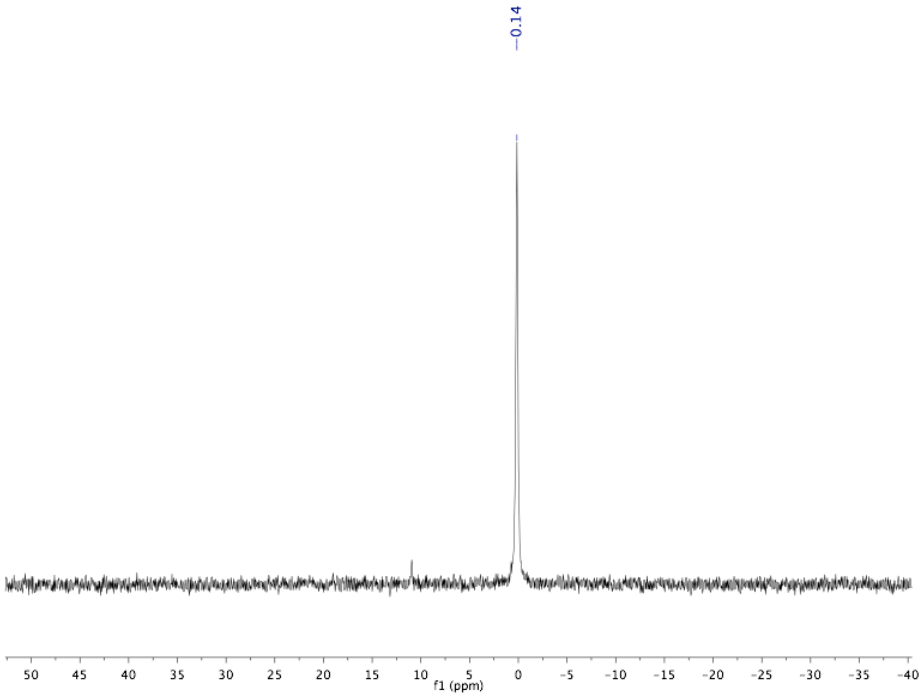


Figure S48. $^{31}P\{^{1}H\}$ NMR.

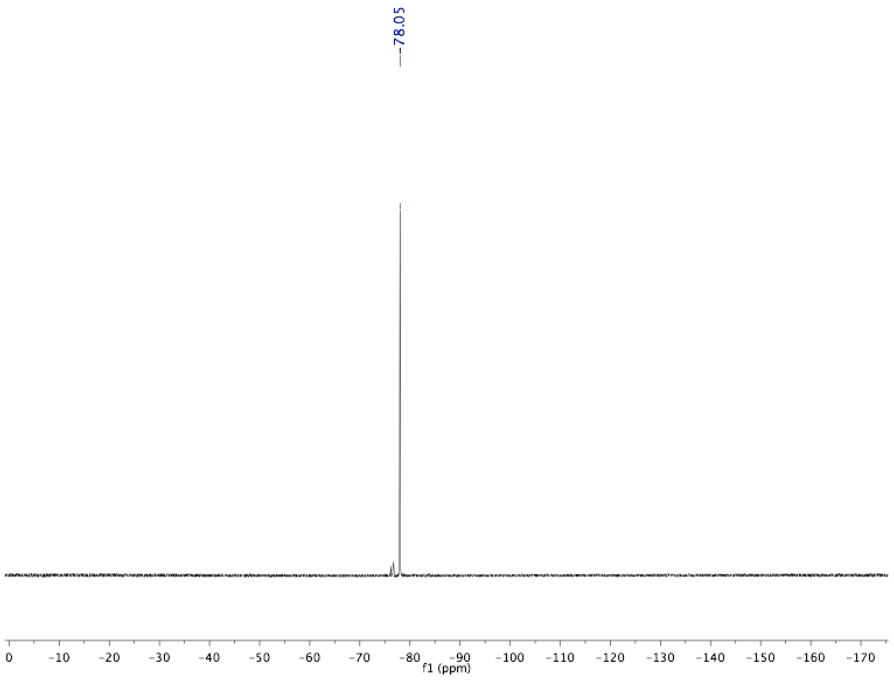


Figure S49. ^{19}F NMR.

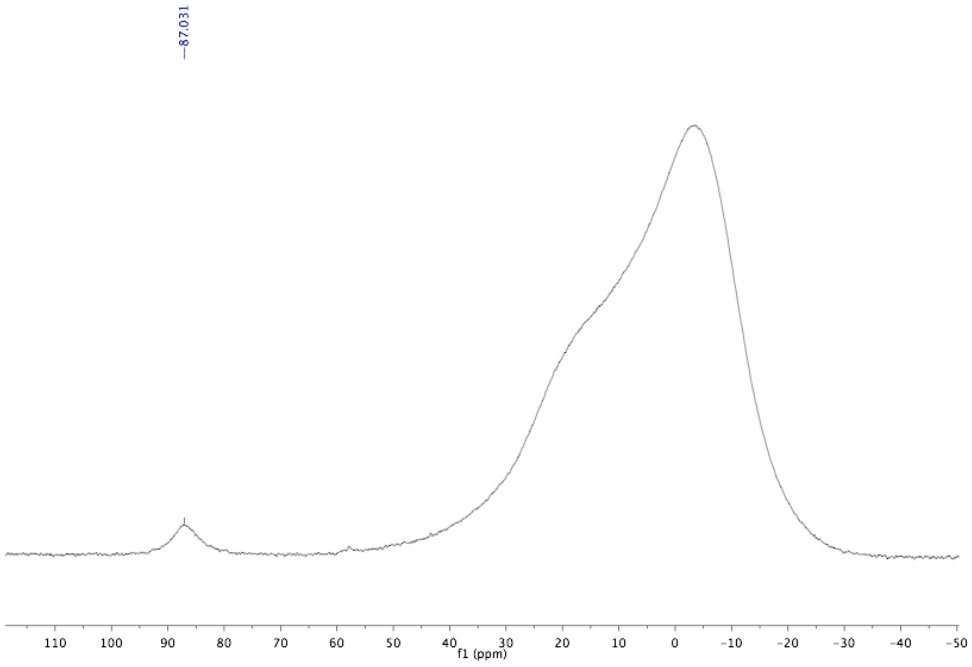


Figure S50. $^{11}B\{^{1}H\}$ NMR.

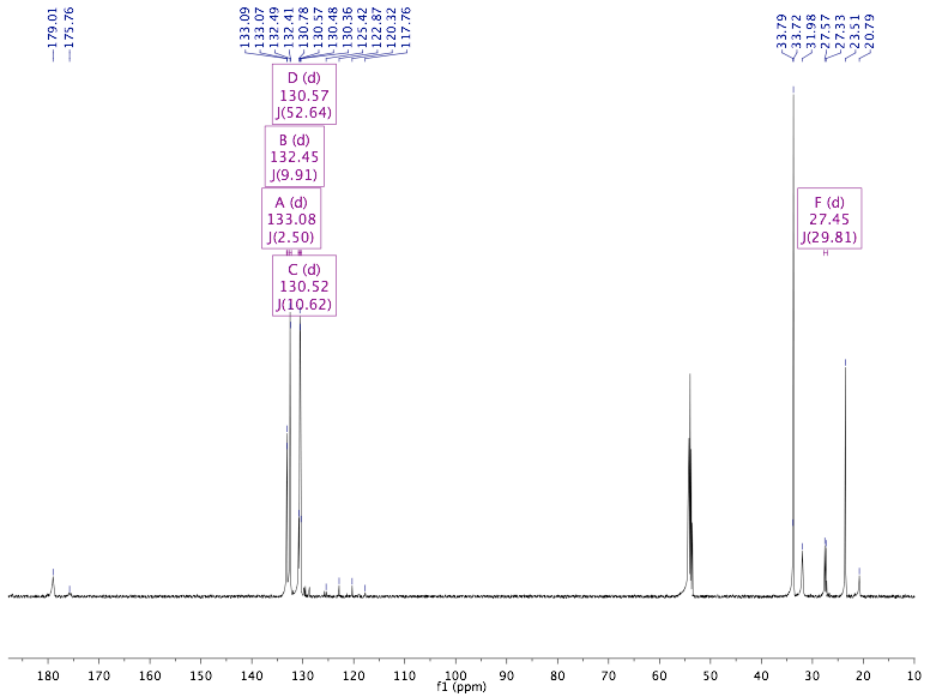


Figure S51. $^{13}C\{^{1}H\}$ NMR.

Synthesis of *trans*-[(PPh_3)($Ph_2P(CH_2)_2B(C_8H_{14})$)$Re(CO)_4$][OTf] ([1-$E_1Ph_1$][OTf]).

Under the nitrogen atmosphere of a glovebox a 20 mL scintillation vial was charged with 819 mg (1.19 mmol) *trans*-(PPh_3)$Re(CO)_4I$ and 10 mL CH_2Cl_2. Solid AgOTf (382 mg, 1.49 mmol, 1.25 equiv) was added, and the reaction mixture was stirred for 2 hours with protection from light. The resulting cloudy mixture was filtered through celite to give a clear, pale yellow solution. A 100 mL Teflon-stoppered pressure tube was charged with the filtrate, and a solution of 398 mg (1.19 mmol) $Ph_2P(CH_2)_2B(C_8H_{14})$ in 5 mL CH_2Cl_2 was added, along with a stirbar. The tube was sealed, removed from the glovebox, and heated in an oil bath to 60 °C for 24 hours. After the allotted time, the reaction was cooled to ambient temperature and returned to the box. The reaction mixture was filtered and the solvent were removed *in vacuo*, giving 1.21 g (1.15 mmol, 97%) pure white [**1-E_1Ph_1**][OTf]. **^{1}H NMR** (CD_2Cl_2, 500 Mhz): δ 1.10-1.18 (m, 2H), 1.34 (dd, *J*

= 10.2, 16.4, 2H, $Ph_2PCH_2CH_2B(C_8H_{14})$), 1.52-1.62 (m, 4H), 1.68 (br s, 2H), 1.77-1.88 (m, 6H), 3.00 (dd, J = 7.3, 15.6, 2H $Ph_2PCH_2CH_2B(C_8H_{14})$,7.46-7.52 (m, 6H), 7.54-7.62 (m, 19H). **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2, 121 MHz): δ 0.6 (d, J_{PP} = 80.6 Hz, 1P), 5.7 (d, J_{PP} = 80.0 Hz, 1P). **^{19}F NMR** (CD_2Cl_2, 282 MHz): δ -77.9. **$^{11}B\{^1H\}$ NMR** (CD_2Cl_2, 160 MHz): δ 88.5. **$^{13}C\{^1H\}$ NMR** (CD_2Cl_2, 125 MHz): δ 20.97 (br, $Ph_2PCH_2CH_2B(C_8H_{14})$), 23.51, 28.68 (d, J_{PC} = 30.6 Hz $Ph_2PCH_2CH_2B(C_8H_{14})$), 32.0 (br), 33.71, 121.55 (q, J_{CF} = 320 Hz, $CF_3SO_3^-$), 129.72 (d, J_{PC} = 10.5 Hz), 130.07 (d, J_{PC} = 11.0 Hz), 130.20, 132.26 (dd, J_{PC} = 2.1, 22.1 Hz), 132.35 (d, J_{PC} = 9.8 Hz), 132.54 (dd, J_{PC} = 2.4, 12.2 Hz), 132.76, 133.23 (d, J_{PC} = 11.3 Hz), 133.81 (d, J_{PC} = 11.0 Hz), 185.96 (t, J_{PC} = 7.5 Hz, CO). **IR (CH_2Cl_2):** υ_{CO}, 2000 cm^{-1}. **HRMS** (TOF ES^+): m/z cald for $C_{44}H_{43}BO_4P_2Re$: 895.2297. Found: 895.2271.

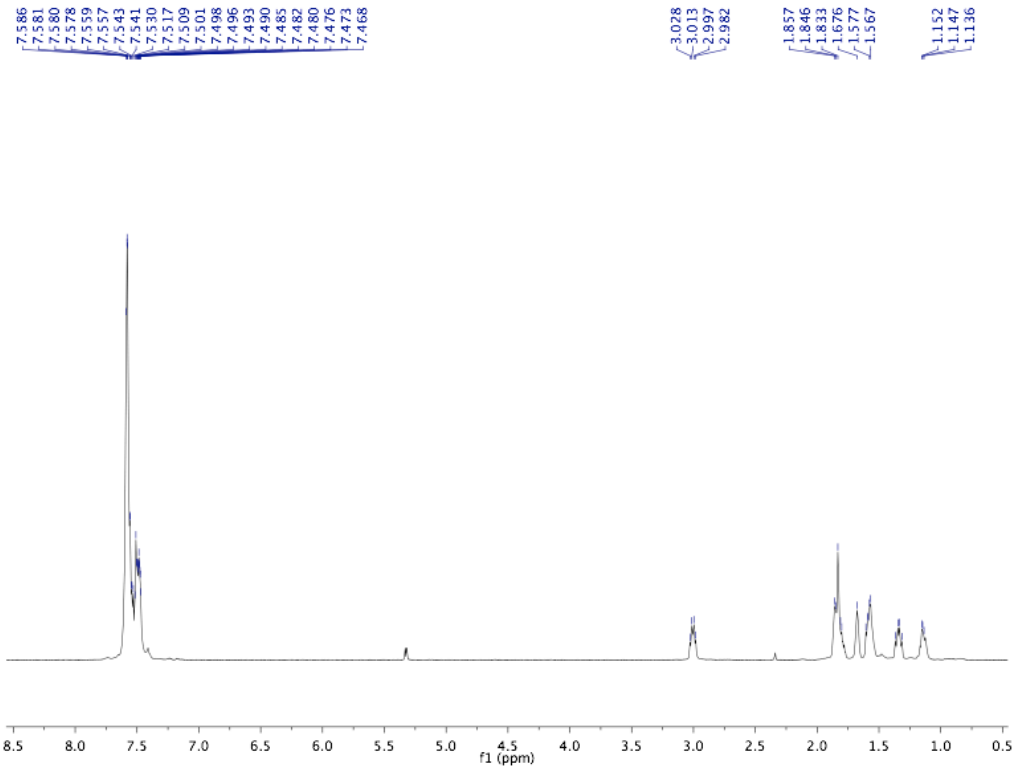


Figure S52. ^1H NMR.

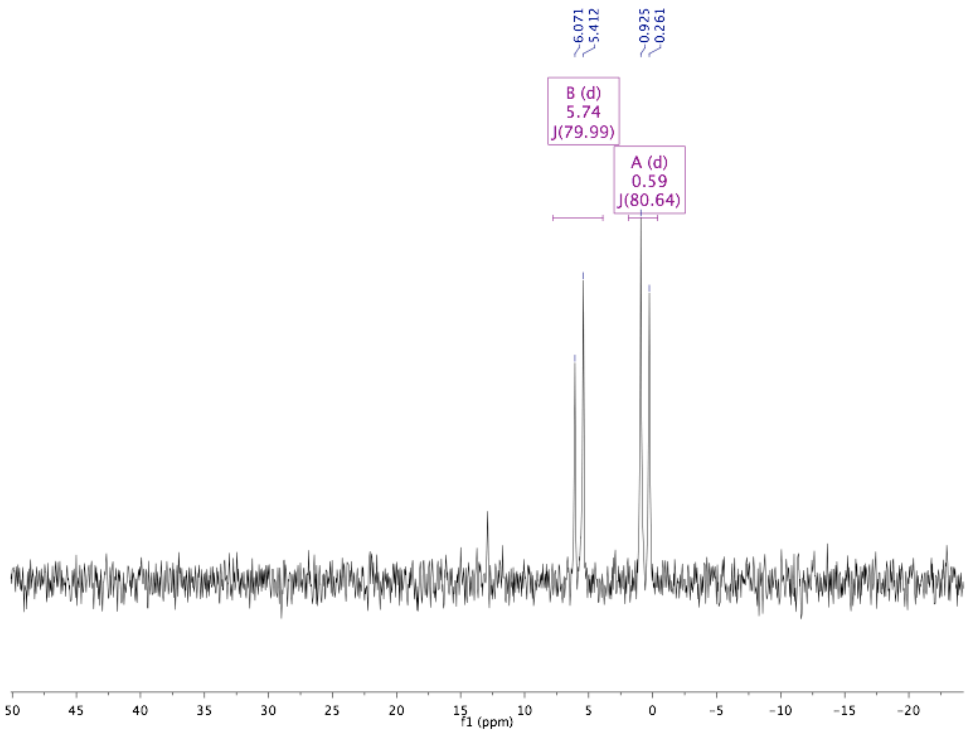


Figure S53. $^{31}P\{^{1}H\}$ NMR.

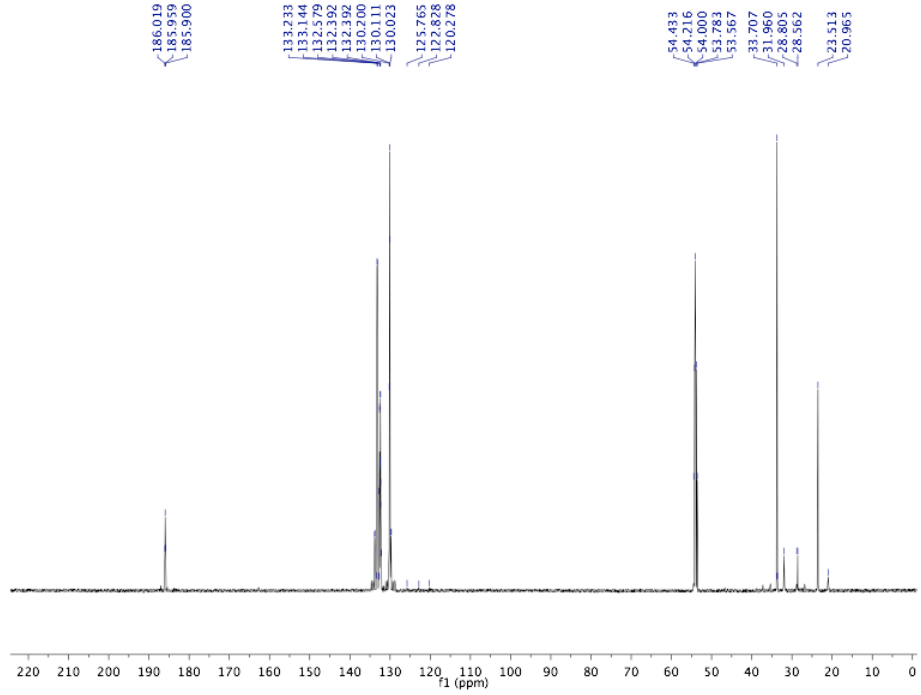


Figure S54. $^{13}C\{^{1}H\}$ NMR:

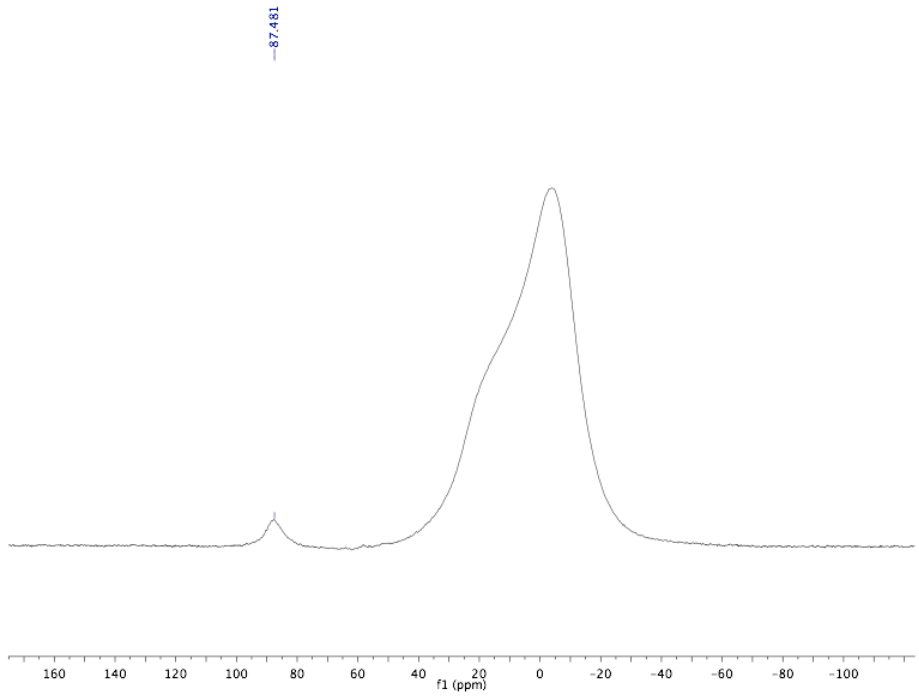


Figure S55. $^{11}B\{^{1}H\}$ NMR (broad underlying signal is borosilicate in probe construction).

Synthesis of $[Ph_2PCH_2CHCH_2Re(CO)_5][OTf]$.

A 60 mL glass pressure vessel fitted with a Teflon valve was charged with 0.247 g (1.09 mmol) allyldiphenylphosphine ($Ph_2PCH_2CHCH_2$), 0.518 g (1.09 mmol) $Re(CO)_5OTf$, 15 mL CH_2Cl_2, and a stirbar. The vessel was sealed and heated to 60 °C for 11 hours with stirring, after which time the vessel was cooled to ambient temperature, and moved to a glovebox. The colorless solution was filtered, and the solvents removed *in vacuo*, affording 0.730 g (1.04 mmol, 95%) spectroscopically pure white powder. **^{1}H NMR** (CD_2Cl_2, 300 MHz): δ 3.68 (dd, J_{HH} = 5.8 Hz, J_{PH} = 10.34 Hz, 2H, $Ph_2PCH_2CHCH_2$), 5.25-5.5 (m, 3H, $Ph_2PCH_2CHCH_2$), 7.5-7.67 (m, 10H, $Ph_2PCH_2CHCH_2$). **^{31}P{^{1}H} NMR** (CD_2Cl_2, 121 MHz) δ: -5.0 (br s). **^{19}F NMR** (CD_2Cl_2, 282 MHz): δ -79.4. **^{13}C{^{1}H} NMR** (CD_2Cl_2, 126 MHz): δ 37.41 (d, J_{PC} = 31.2 Hz, $Ph_2PCH_2CHCH_2$), 121.60 (q, J_{FC} = 321.1 Hz, $[CF_3SO_3]^-$), 124.85 (d, J_{PC} = 12.8 Hz, $Ph_2PCH_2CHCH_2$), 127.09 (d, J_{PC}

= 5.9 Hz, $Ph_2PCH_2CHCH_2$), 130.37 (d, J_{PC} = 52.7 Hz, *ipso*-$Ph_2PCH_2CHCH_2$), 130.49 (d, J_{PC} = 10.8 Hz, *m*-$Ph_2PCH_2CHCH_2$), 132.51 (d, J_{PC} = 10.2 Hz, *o*-$Ph_2PCH_2CHCH_2$), 133.24 (d, J_{PC} = 2.5 Hz, *p*-$Ph_2PCH_2CHCH_2$), 175.68 (br d, J_{PC} = 38 Hz, axial *C*O), 178.69 (br s, eq. *C*O). **IR** (CD_2Cl_2): υ_{CO}, 2157 (m), 2098 (w), 2048 (vs) cm^{-1}; υ_{SO}, 1270 (m) cm^{-1}; υ_{CF}, 1161 (w) cm^{-1}. **HRMS** (FAB$^+$): m/z calcd. for $[C_{20}H_{15}ReO_5P]^+$: 553.0215. Found: 553.0222 (M^+), 525.0161 (M-CO), 497.0260 (M-2CO), 469.0208 (M-3CO).

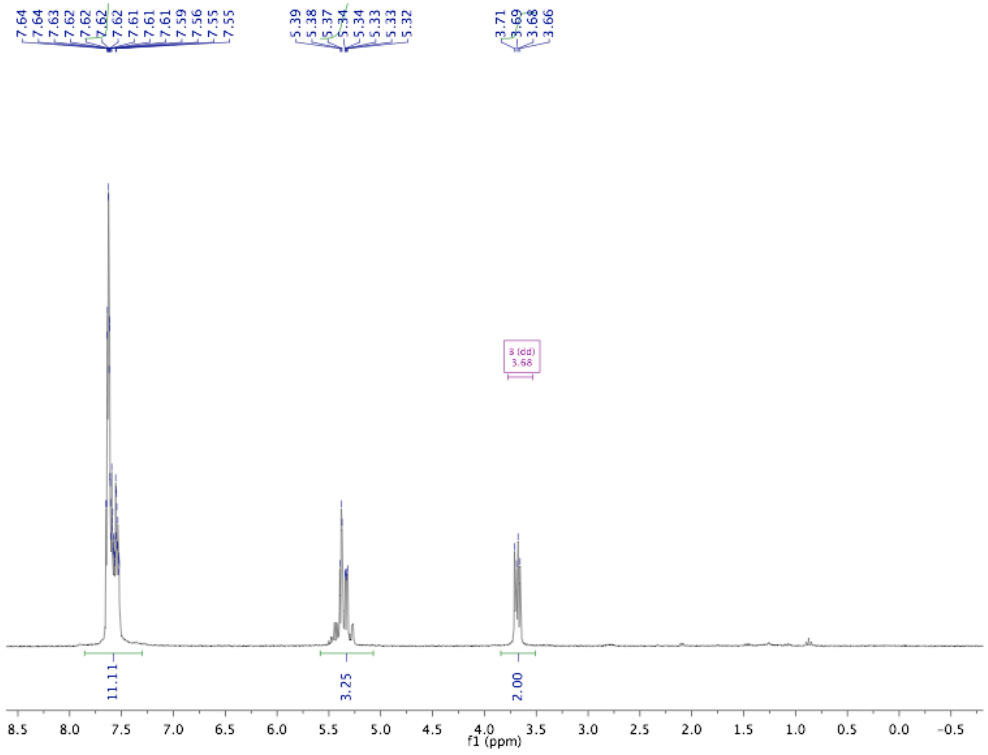


Figure S56. ^{1}H NMR.

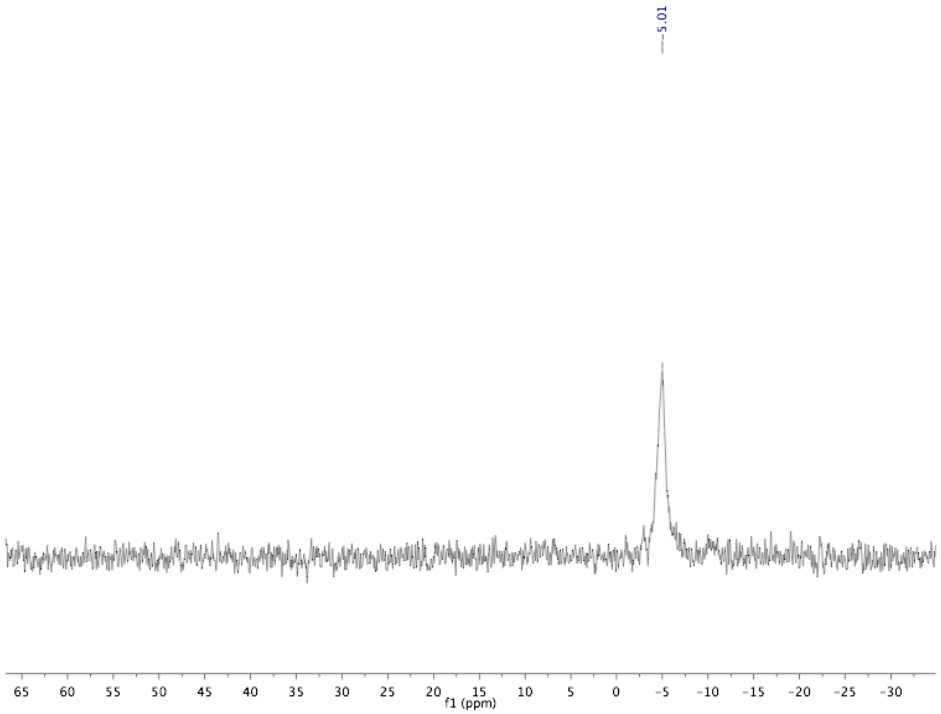


Figure S57. $^{31}P\{^{1}H\}$ NMR.

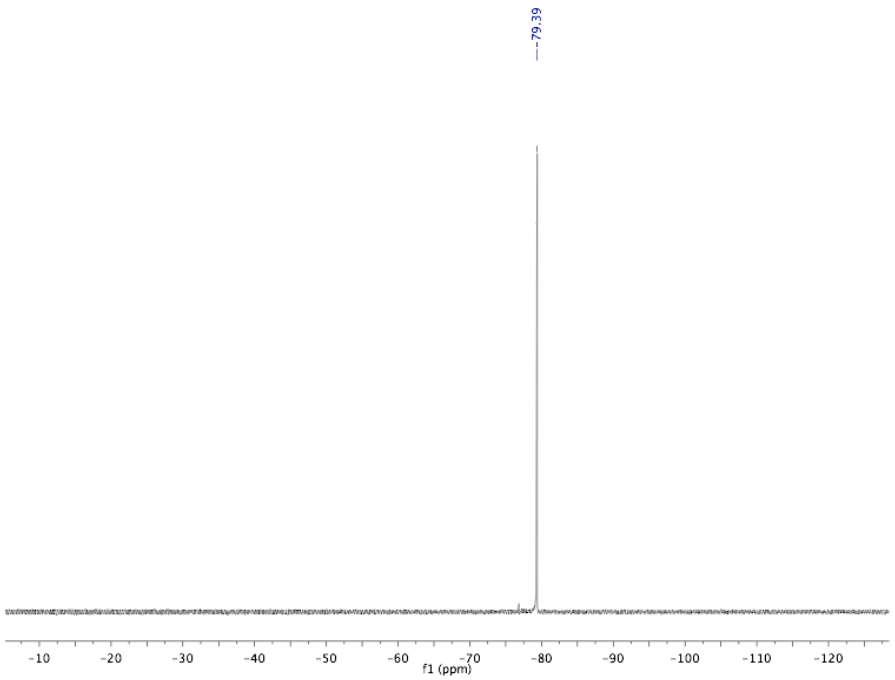


Figure S58. ^{19}F NMR.

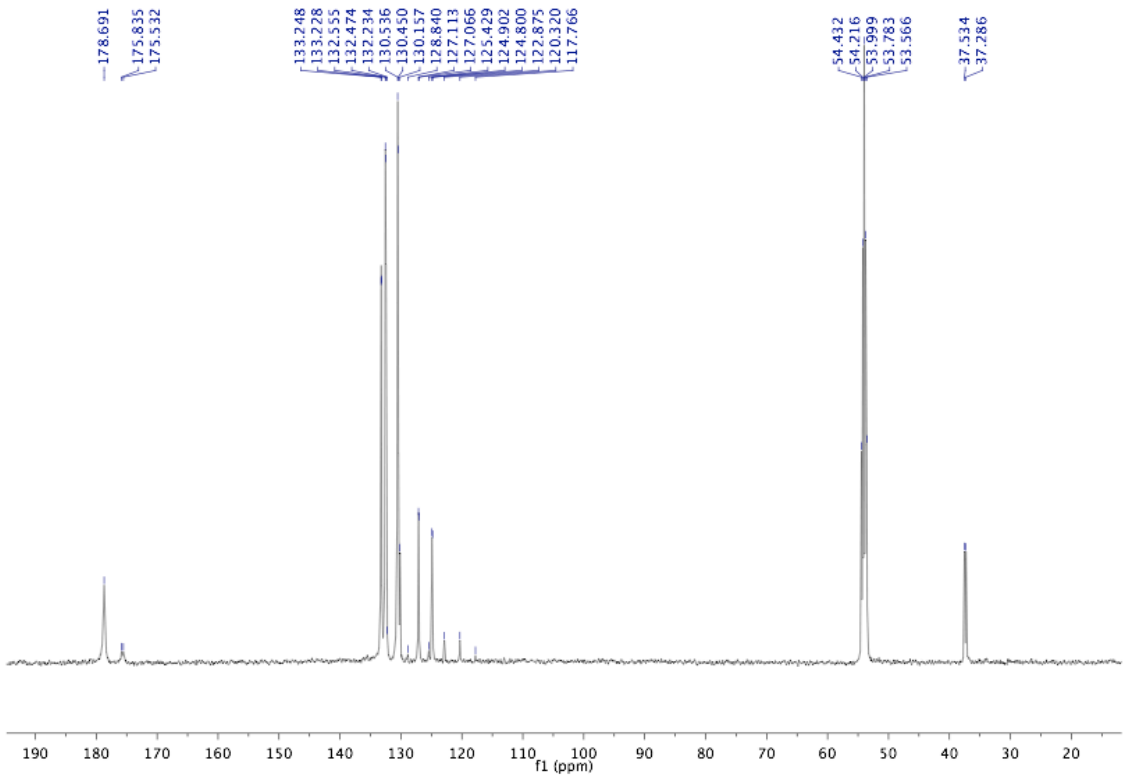


Figure S59. $^{13}C\{^{1}H\}$ NMR.

Synthesis of [($Ph_2P(CH_2)_3B(C_8H_{14})$)$Re(CO)_5$][OTf] ([1-$P_1$][OTf]).

A 20 mL glass pressure vessel fitted with a Teflon valve was charged with 0.710 g (1.01 mmol) [$Ph_2PCH_2CHCH_2Re(CO)_5$][OTf], 0.124 g (1.01 mmol) 9-BBN, 5 mL CH_2Cl_2, and a magnetic stirbar. The vessel was sealed, removed from the box and heated to 60 °C for 12 hours. After this time the clear colorless solution was cooled to ambient temperature, brought back into the glovebox, and filtered. Removal of solvents from the filtrate yielded 0.747 g (0.91 mmol, 90%) of a white powder, which was ~95% pure by ^{1}H NMR, with the other 5% being unreacted starting material. Treatment under the same conditions with slightly more 9-BBN gave spectroscopically pure [**1-P_1**][OTf] after washing with pentane. Analytically pure material was obtained by crystallization from a THF solution layered (1:1) with pentane at -35 °C. **^{1}H NMR**

(C_6D_5Cl, 300 MHz): δ 1.08 (br m, 2H), 1.48 (br m, 8H), 1.70 (br m, 6H), 1.84 (br s, 2H), 2.82 (br m, 2H), 7.16-7.23 (m, 2H), 7.26-7.33 (m, 4H), 7.45-7.54 (m, 4H). **$^{31}P\{^1H\}$ NMR** (C_6D_5Cl, 121 MHz): δ -6.2. **^{19}F NMR** (C_6D_5Cl, 282 MHz): δ -78.2. **$^{13}C\{^1H\}$ NMR** (CD_2Cl_2, 125 Hz): δ 20.3, 23.6, 26.1, 29.0 (br), 31.6 (br), 33.6, 34.6 (d, J_{PC} = 30.0 Hz), 121.6 (q, J_{FC} = 321.0 Hz, $SO_3CF_3^-$), 130.5 (d, J_{PC} = 53.5 Hz), 130.5 (d, J_{PC} = 10.7 Hz), 132.2 (d, J_{PC} = 10.2 Hz), 133.1 (d, J_{PC} = 2.2 Hz), 175.8 (br, axial CO), 178.9 (br, equatorial CO). **$^{11}B\{^1H\}$ NMR** (CD_2Cl_2, 160 MHz): δ 87.4. **IR** (CH_2Cl_2): υ_{CO}, 2156 (m), 2095 (w), 2047 (vs) cm^{-1}. **Anal. Calcd.** for $C_{29}H_{30}BF_3O_8PReS$: C, 42.29; H, 3.74. Found: C, 42.08; H, 3.74.

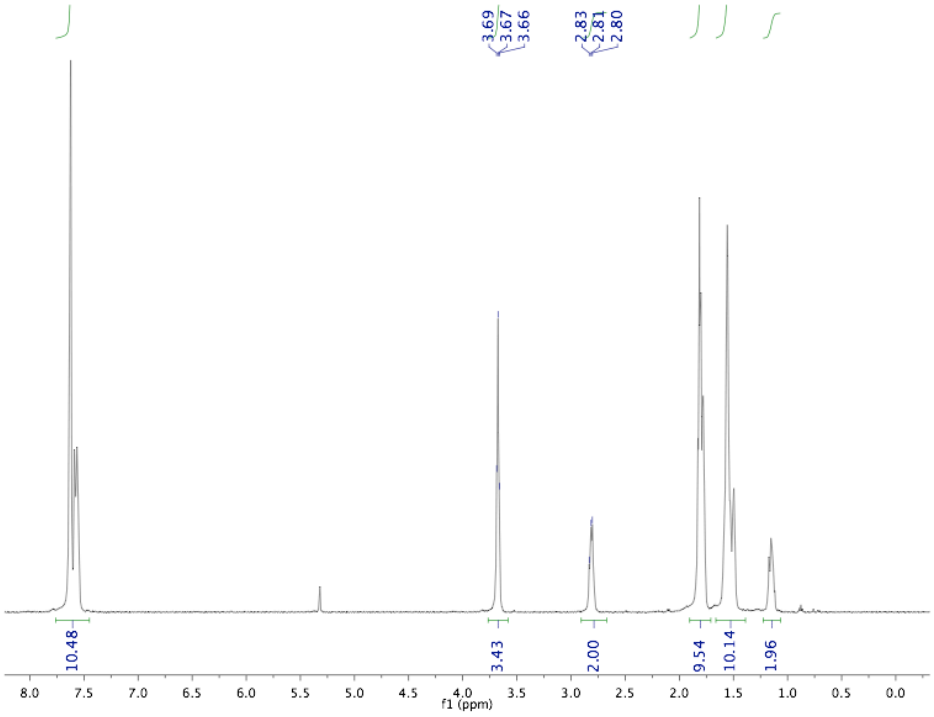


Figure S60. ^1H NMR (1 THF of crystallization).

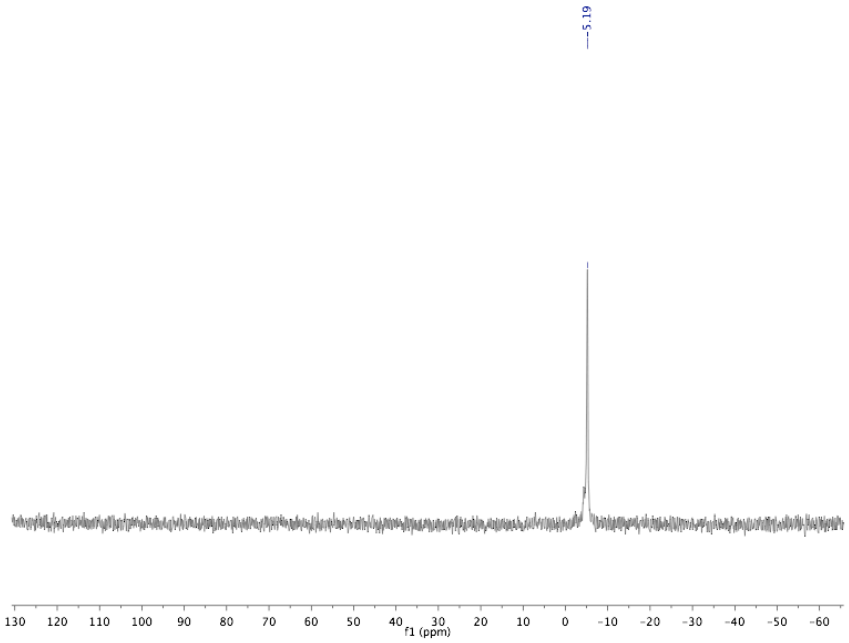


Figure S61. $^{31}P\{^{1}H\}$ NMR.

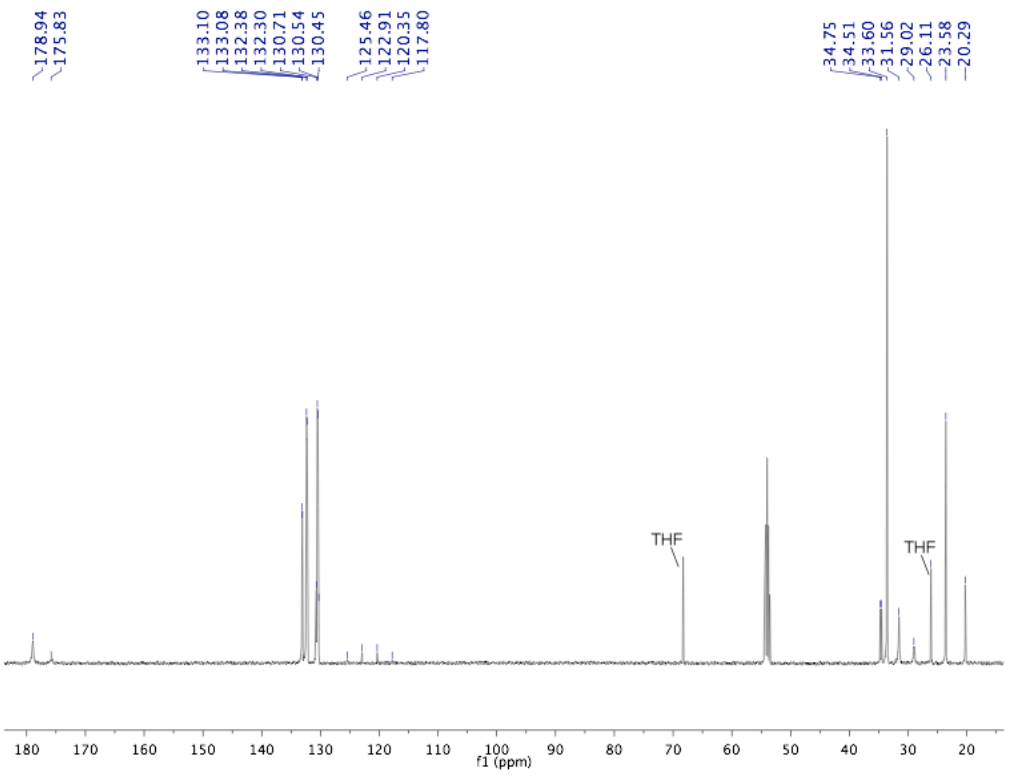


Figure S62. $^{13}C\{^{1}H\}$ NMR (1 THF of crystallization).

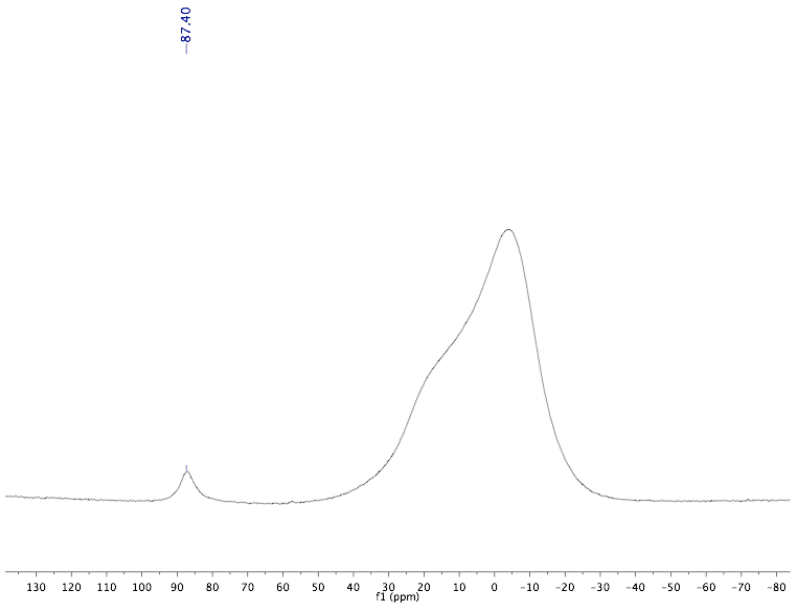


Figure S63. $^{11}B\{^{1}H\}$ NMR (broad underlying signal is borosilicate in probe construction).

General procedure for preparation of BAr^{F}_{4} salts of rhenium complexes.

The appropriate rhenium cation, bearing either a BF_4 or OTf counter anion, was dissolved in CH_2Cl_2 solution (affording roughly 20 mM concentration) with stirring. Solid $NaBArF_4$ (1 equiv relative to Re complex) was added, and the mixture stirred for at least 2 hours. Following filtration, the solvents were removed from the filtrate *in vacuo* to afford powders or oils of the rhenium BAr^{F}_{4} salts. If the product was oily, it was triturated with pentane to give a powder, and the pentane was removed under vacuum. Yields were essentially quantitative, and spectroscopic analysis correlated very favorably with the BF_4 or OTf starting materials, indicating that the structure had not changed. ^{19}F NMR unequivocally showed removal of BF_4 or OTf, and incorporation of BAr^{F}_{4} anion.

IV. Hydride Reductions of Bis(phosphine) Cations.

A. Reductions of *trans*-[$(Ph_2PCH_2B(C_8H_{14}))_2Re(CO)_4$][$B(C_6F_5)_4$] ([1-$M_2$][$B(C_6F_5)_4$]).

NMR-scale Reaction of [1-M_2][$B(C_6F_5)_4$] with 1 equiv [HPt][PF_6].

To a stirring ~0.6 mL C_6D_5Cl solution of 31.3 mg (0.0194 mmol) [**1-M$_2$**][$B(C_6F_5)_4$] was added 12.4 mg (0.0194 mmol) [**HPt**][PF_6]. Monitoring by NMR spectroscopy showed a slow reaction, with ~50% conversion after 12 hours, ~70% conversion after 24 hours, and ~90% conversion after 6 days.

Reaction of [1-M_2][$B(C_6F_5)_4$] with 1 equiv [HPt][PF_6] in the presence of [Na][BF_4].

A 20 mL scintillation vial was charged with 103.0 mg (0.0637 mmol) [**1-M$_2$**][$B(C_6F_5)_4$], 35.0 (0.319 mmol, 5 equiv) $NaBF_4$, and 2 mL C_6H_5Cl. With stirring, 49.0 mg (0.0764, 1.2 mmol) [**HPt**][PF_6] was added slowly as a solid. The mixture turned yellow and developed precipitates over a few minutes, and was stirred overnight. The reaction mixture was filtered, and the solvent removed from the filtrate under vacuum. The solids were extracted with C_6H_6, filtered, and the solvents removed from the filtrate to afford 59 mg (99%) **2-M$_2$** as a pale yellow powder in ~95% purity ([**HPt**]$^+$ was the other observed species, along with small amounts of residual C_6H_5Cl). **^{1}H NMR** (C_6D_6, 300 MHz): δ 1.49 (br, $Ph_2PCH_2B(C_8H_{14})$), 1.88 (br, $Ph_2PCH_2B(C_8H_{14})$), 7.16 ($Ph_2PCH_2B(C_8H_{14})$, 12H), 7.53 (br, $Ph_2PCH_2B(C_8H_{14})$, 8H), 13.96 (t, J_{PH} = 6.0 Hz, Re-C*H*O, 1H). **^{31}P{^{1}H} NMR** (C_6D_6, 121 MHz): δ -2 (br, 1P), 6.0 (br, 1P). **IR** (heptane): ν_{CO} 1999 (s), 1950 (s), 1938 (s) cm^{-1}.

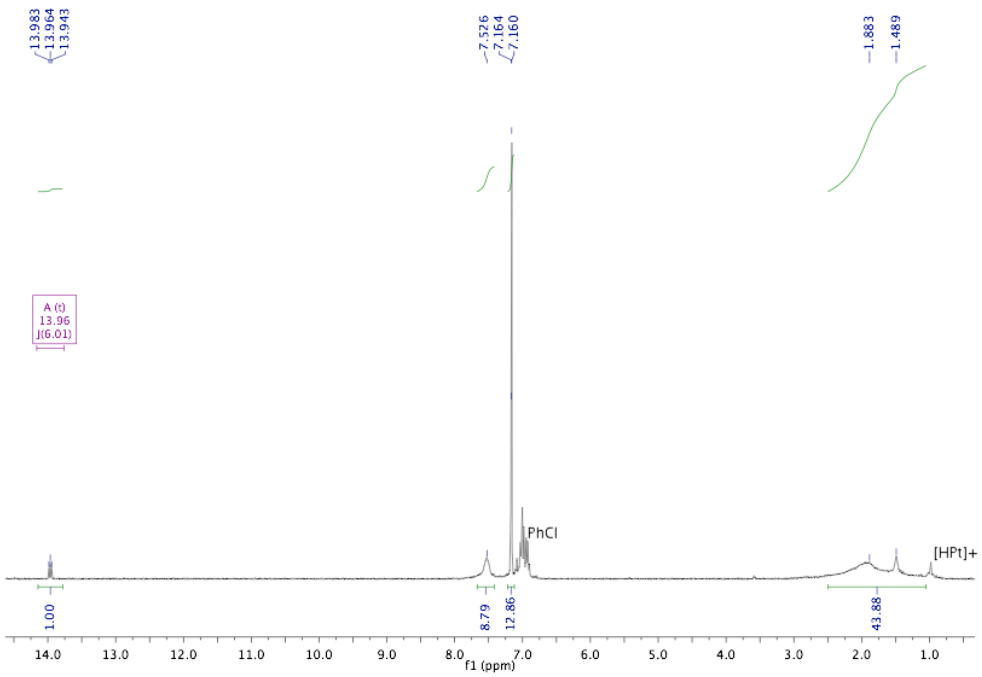


Figure S64. ^{1}H NMR.

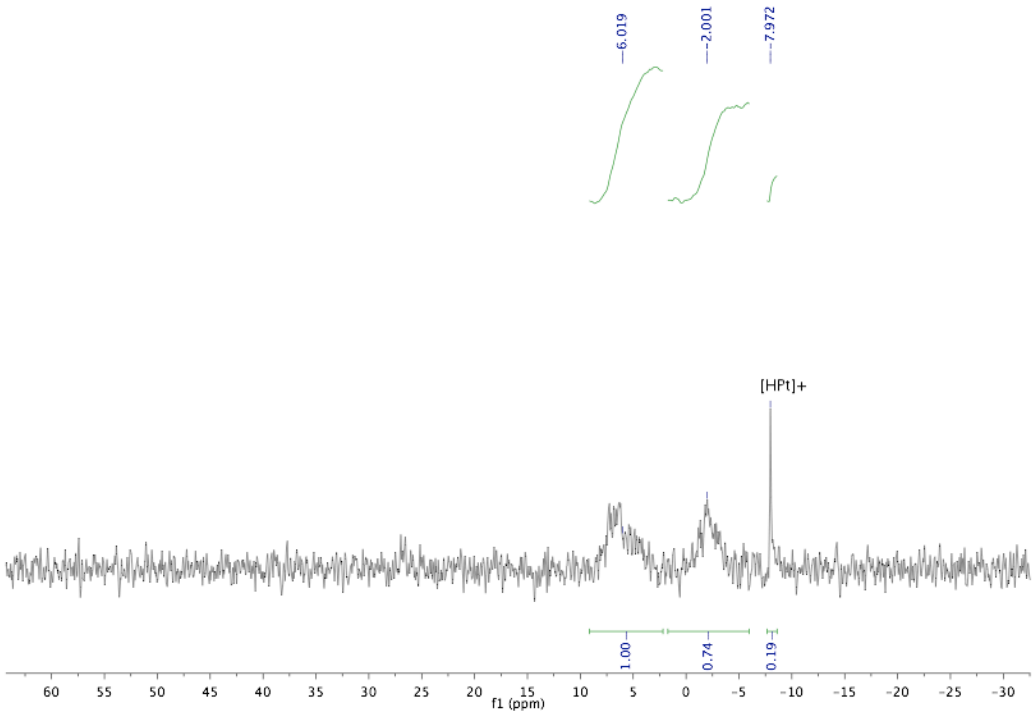


Figure S65. $^{31}P\{^{1}H\}$ NMR.

NMR-scale reaction of [1-M_2][$B(C_6F_5)_4$] with 1 equiv [HPt][PF_6] in the presence of [$hept_4N$][BF_4].

A small vial was charged with 29.1 mg (0.0180 mmol) [**1-M_2**][$B(C_6F_5)_4$], 17.7 mg (0.0360 mmol, 2 equiv) tetraheptylammonium tetrafluoroborate, and ~0.6 mL C_6D_5Cl. With stirring, 11.6 mg (0.0180 mmol, 1 equiv) [**HPt**][PF_6] was added as a solid. The mixture was moved to a J-Young tube, and allowed to sit for about 3 hours, at which point NMR spectroscopy showed near complete conversion to the desired boroxycarbene. As in the isolated product, at room temperature many resonances were quite broad, including the ^{31}P NMR. Variable temperature NMR studies were therefore undertaken.

Variable Temperature NMR spectroscopy:

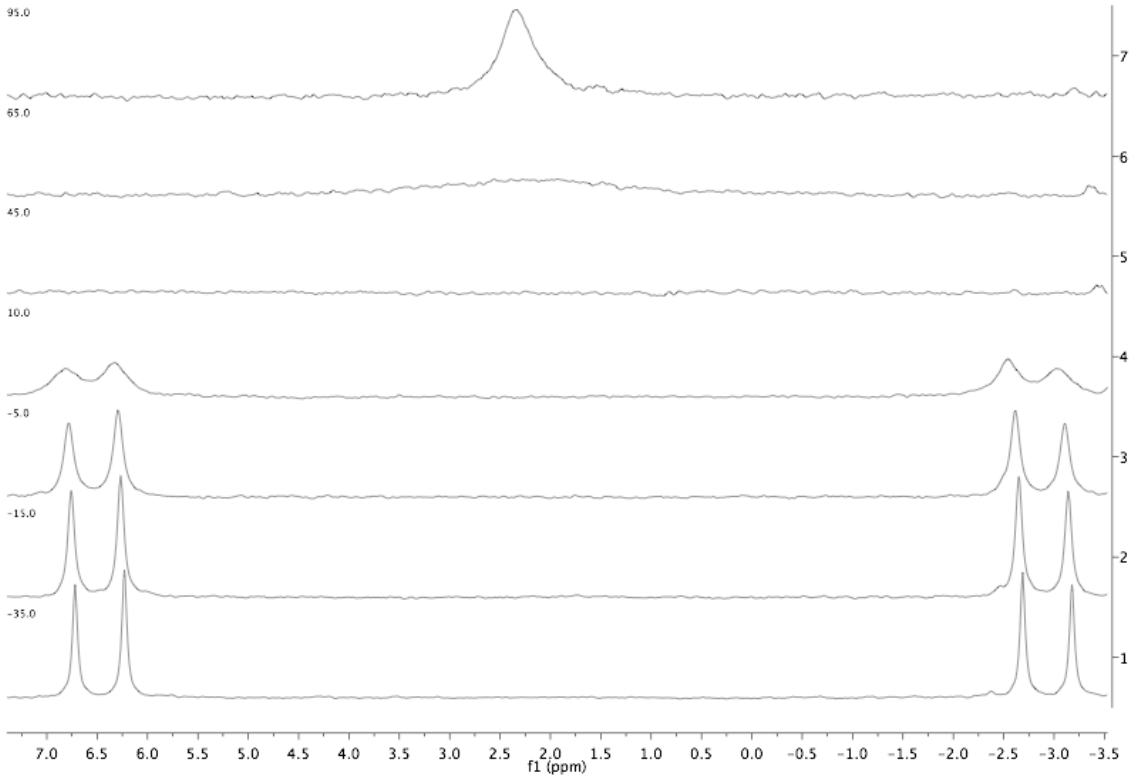


Figure S66. $^{31}P\{^1H\}$ NMR from -35 to 95 C.

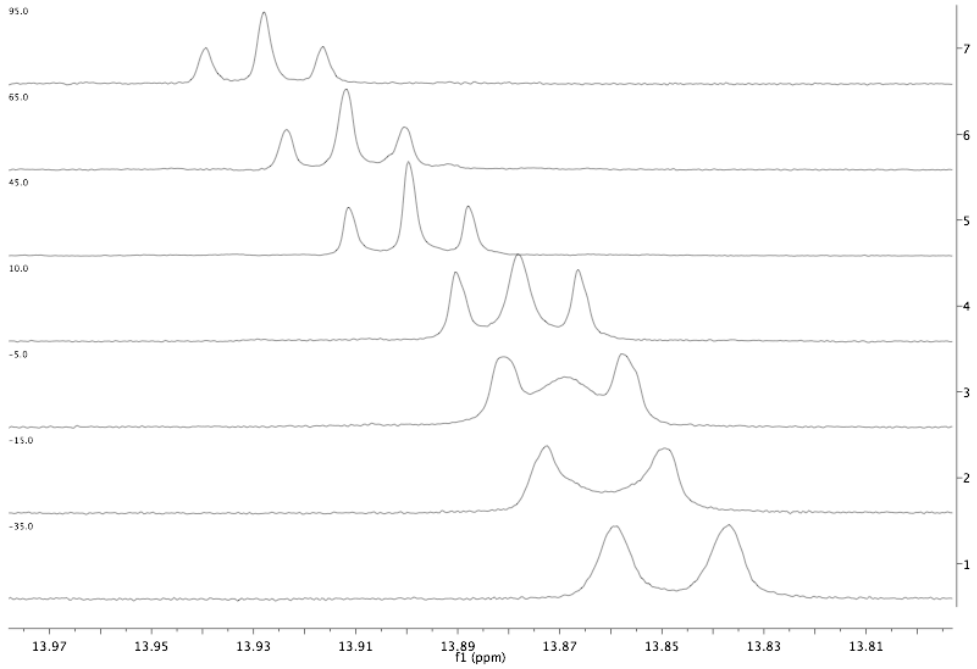


Figure S67. ^{1}H NMR (formyl region) from -35 to 95 C.

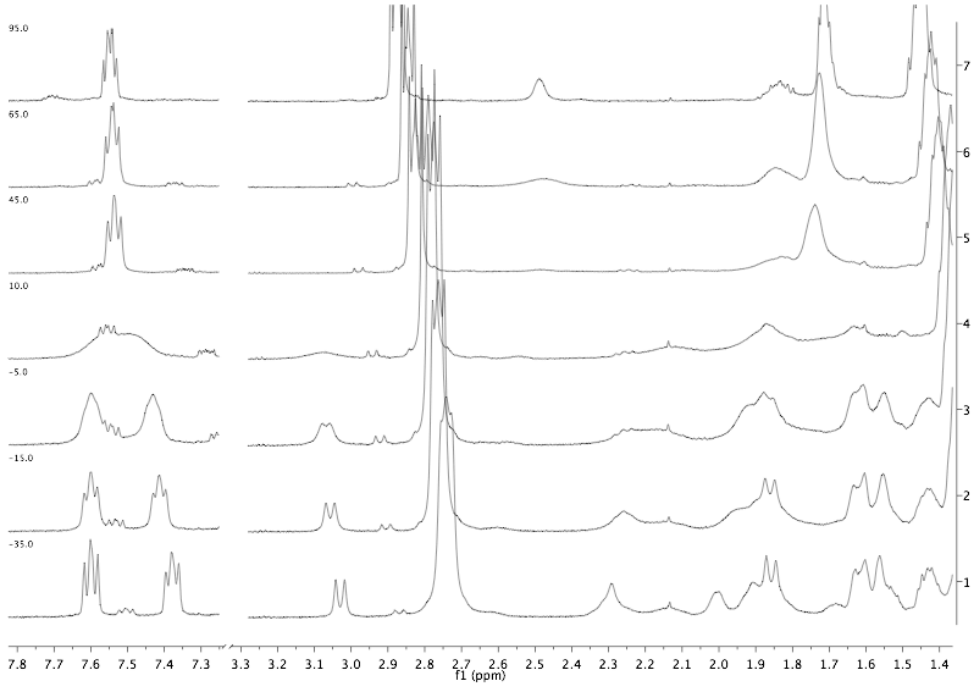
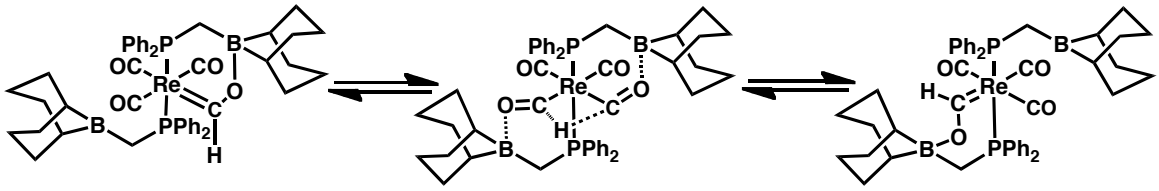


Figure S68. ^{1}H NMR (aryl, alkyl regions from -35 to 95 C).



Scheme S2.

Variable temperature NMR studies of **2-M$_2$** between -35 °C and +95 °C in C_6D_5Cl revealed fluxional processes. The ^{31}P NMR spectrum of **2-M$_2$** displays two sharp doublets (δ -2.9, $^2J_{PP}$ = 99.1 Hz; δ 6.5, $^2J_{PP}$ = 99.2 Hz) at low temperatures, which coalesce into a singlet (δ 2.3) at ~50 °C. The ^{1}H NMR spectrum shows similar sharpening upon cooling to -35 °C, with two sharp doublets at δ 3.07 (J_{PH} = 12.1 Hz) and δ 1.87 (J_{PH} = 13.1 Hz) emerging for two inequivalent CH_2 groups on the ligands. Near 50 °C these doublets coalesce into one broad singlet, consistent with the fluxional processes that give a more symmetric ligand environment. Interestingly, the carbene proton triplet collapses into a doublet as it is cooled, δ 13.85, J_{PH} = 11.1 Hz. This is consistent with a static structure with *intramolecular* coordination of one pendant borane to the carbene oxygen, in contrast to ethylene-linker-containing complex **2-E$_2$**, which has intermolecular coordination and is dimeric. The restricted rotation of the carbene affords favorable angles for P-H coupling to the phosphinoborane that is binding the oxygen, while the other phosphine has an undetectable coupling constant due to the unfavorable coupling angles. The phosphine resonance at δ -2.9 is assigned as the intramolecularly coordinated phosphinoborane, due to the slight upield shift consistent with a 6-membered ring structure, and from ^{1}H-^{31}P gHMBC correlation to the carbene proton, as well as the downfield-shifted methylene protons of that ligand (also consistent with a constrained ring geometry).

From the coalescence temperature the barrier for the fluxtional process can be estimated, $\Delta G^{\ddagger}$ = 13.6 ± 0.2 kcal/mol (323 K). The exact process that creates equivalent ligand

environments could be B-O bond breaking, rotation, and B-O bond formation with the other ligand. $^{13}C\{^{1}H\}$ NMR spectroscopy is not entirely consistent with this, however, as the CO carbons are very broad at room temperature, implicating exchange of H between the various CO groups of the complex. Further, treatment of carbene **2-M$_2$** with up to 100 equivalents of pyridine leads to *no B-O cleavage*, contrasting the easily broken B-O bonds of external Lewis acids and other linkers. If B-O cleavage were occurring rapidly on the NMR time scale, pyridine binding would be expected to be favored. Transfer of hydride from a formyl to an adjacent carbonyl ligand has been observed before, and that process, which would lead to broadening of CO signals in the ^{13}C NMR, is consistent with our observations (Scheme S2).[13]

NMR-scale Reaction of [1-M$_2$][B(C$_6$F$_5$)$_4$] with 2 equiv [HPt][PF$_6$] in the presence of [hept$_4$N][BF$_4$].

To a stirring ~0.6 mL THF-d_8 solution of 35.4 mg (0.0219 mmol) [**1-M**$_2$][B(C$_6$F$_5$)$_4$] was added 28.1 mg (0.0438 mmol, 2 equiv) [**HPt**][PF$_6$] partwise slowly. The mixture was stirred for an addition 5 minutes before being transferred to a J-Young NMR tube and monitored by NMR spectroscopy. In the first few hours mainly boroxycarbene **2-M**$_2$ was observed, in addition to the asymmetric doubly-reduced product. The tube was affixed to a rotating motor to ensure good mixing, and spun overnight, at which point only doubly-reduced [**5**]$^-$ and unreacted [**HPt**]$^+$ were observed. A ~70% yield of [**5**]$^-$ from **2-M$_1$** was established by two methods, i) simple NMR integration of Re species relative to [heptyl$_4$N]$^+$ (assuming a constant amount of [heptyl$_4$N]$^+$ in solution) and ii) integration against an internal standard (capillary containing P(2,4,6-C$_6$H$_2$Me$_3$)$_3$). No other Re-containing products were observed in solution or when the precipitates were extracted with CD$_3$CN (only [**Pt**]$^{2+}$ precipitated). Spectroscopic analysis was consistent

with an anionic "confused" alkyl species, containing 2 B-O bonds. Separation from the ammonium salts proved challenging, limiting identification to solution methods. Very similar reactivity was observed when C_6D_5Cl was used as the solvent. **^{1}H NMR** (THF-d_8, 600 MHz): δ 0.28 (br, 2H), 0.54 (br, 1H), 0.69 (br, 1H), 1.1-1.9 (m, overlapping with $[hept_4N]^+$), 2.13 (m, 1H), 2.27 (m, 1H), 3.12 (br d, J_{HH} = 13.0, 1H), 4.63 (br d, J_{HH} = 13.2 Hz, 1H), 7.20-7.35 (m, 12H), 7.52 (t, J = 8.3 Hz, 2H), 7.74 (t, J = 8.5 Hz, 2H), 7.85-7.92 (m, 4H). **^{31}P{^{1}H} NMR** (THF-d_8, 121 MHz): δ 22.3 (d, J_{PP} = 127.5 Hz, 1P), 37.3 (d, J_{PP} = 128.4 Hz). **^{13}C{^{1}H} NMR** (THF-d_8, 151 MHz): δ 21.00 (br), 23.32, 25.94, 26.81, 26.87, 27.07, 28.24 (br), 31.50 (d, J_{PC} = 16.7 Hz, $Ph_2PCH_2B(C_8H_{14})$), 33.07 (d, J_{PC} = 16.1 Hz, $Ph_2PCH_2B(C_8H_{14})$), 34.14, 34.34, 34.94, 35.20, 37.88, 82.2 (v br, Re-O-CH_2-BR_3), 125.3 (v br, *ipso*-$B(C_6F_5)_4$), 127.86, 127.98 (d, J_{PC} = 9.0 Hz), 128.59 (d, J_{PC} = 9.2 Hz), 128.66, 128.29, 129.69, 131.73 (d, J_{PC} = 8.9 Hz), 131.83 (d, J_{PC} = 9.5 Hz), 133.86 (d, J_{PC} = 11.1 Hz), 136.31 (d, J_{PC} = 11.3 Hz), 137.28 (dm, J_{FC} = 247.4 Hz, $B(C_6F_5)_4$), 139.28 (d, J_{FC} = 243.6 Hz, $B(C_6F_5)_4$), 139.68 (d, J_{PC} = 41.7 Hz), 141.10 (d, J_{PC} = 45.7 Hz), 144.80 (d, J_{PC} = 37.8 Hz), 148.17 (d, J_{PC} = 36.6 Hz), 149.33 (d, J_{FC} = 240.0 Hz, $B(C_6F_5)_4$), 197.36 (t, J_{PC} = 8.3 Hz, CO), 198.27 (t, J_{PC} = 8.9 Hz, CO), 199.91 (t, J_{PC} = 4.2 Hz, CO). **IR** (C_6D_5Cl): ν_{CO} 2020 (w), 1932 (s), 1867 (m) cm^{-1}. **HRMS (TOF MS ES$^-$):** m/z calcd for $C_{46}H_{54}B_2O_4P_2Re$, 941.3259. Found, 941.3212.

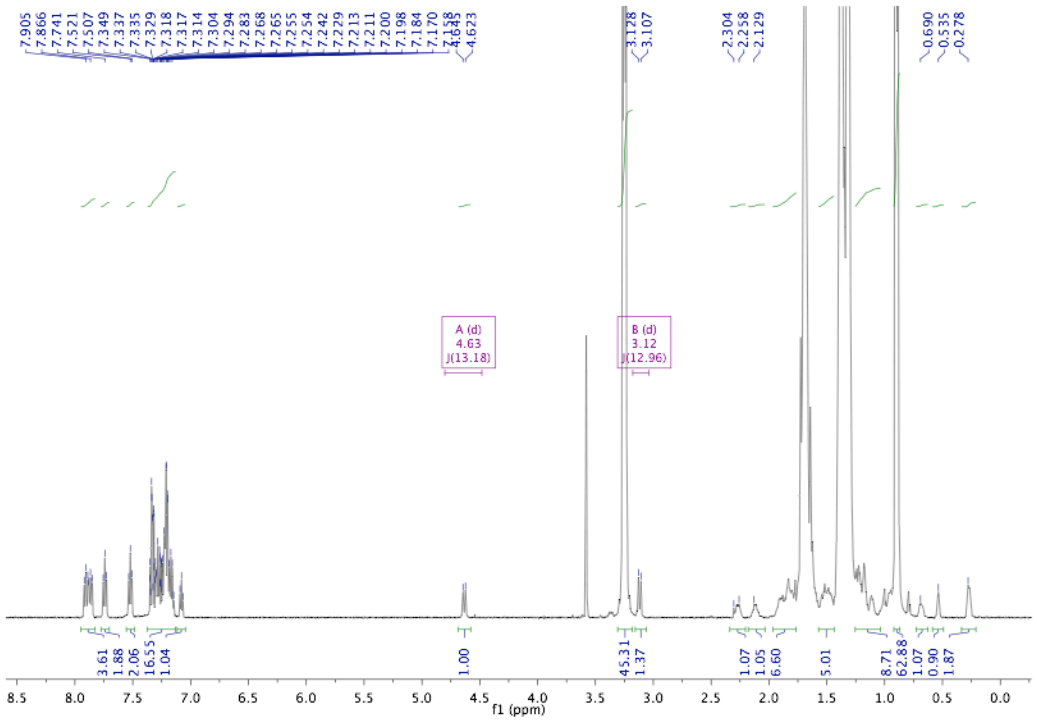


Figure S69. ^{1}H NMR (<1 equiv PhCl impurity).

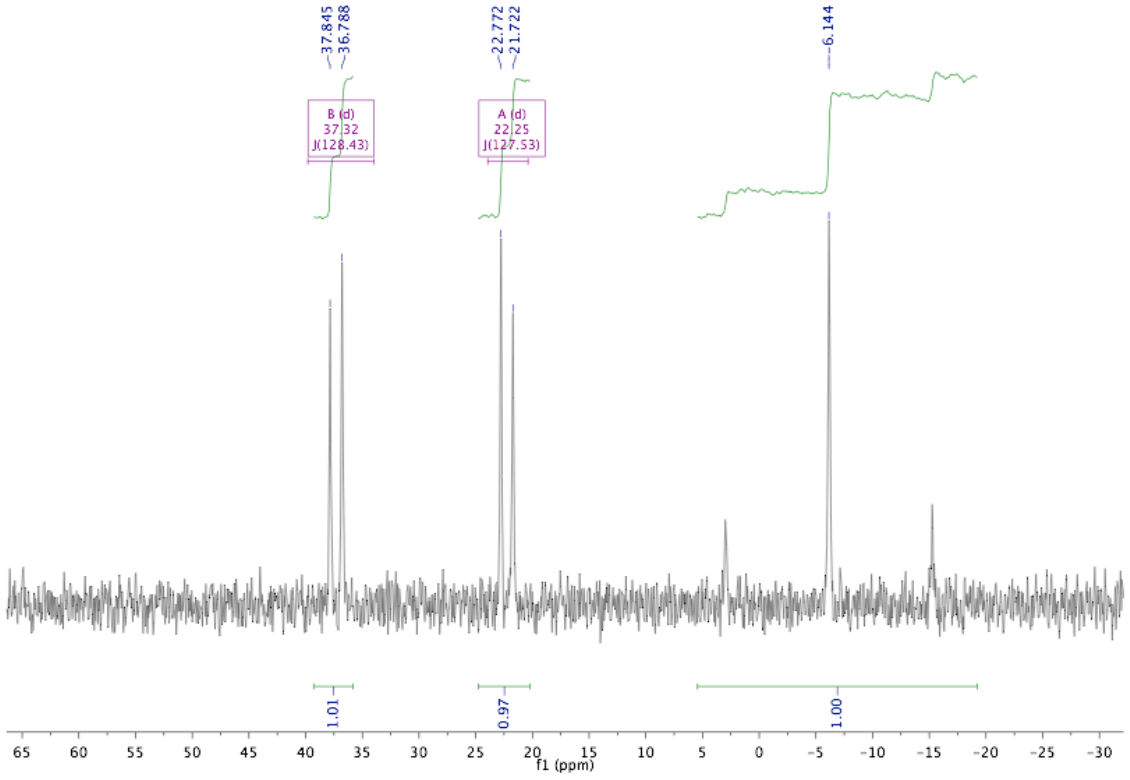


Figure S70. ^{31}P{^{1}H} NMR (singlet with Pt satellites at -6.1 is residual $[HPt]^{+}$).

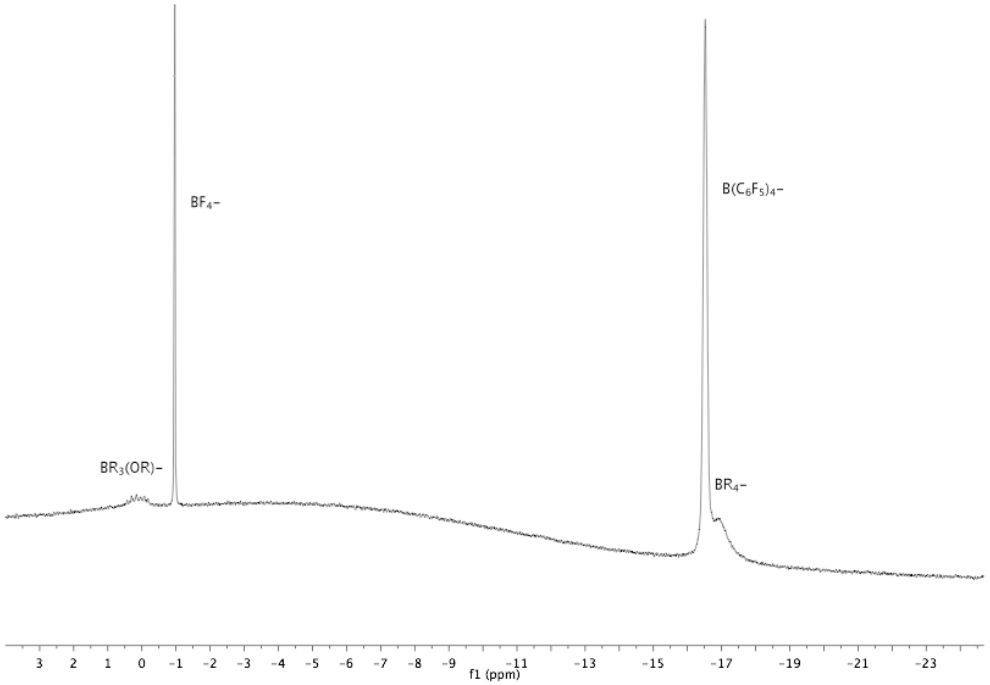


Figure S71. ^{11}B NMR (broad signal in baseline is borosilicate in probe construction).

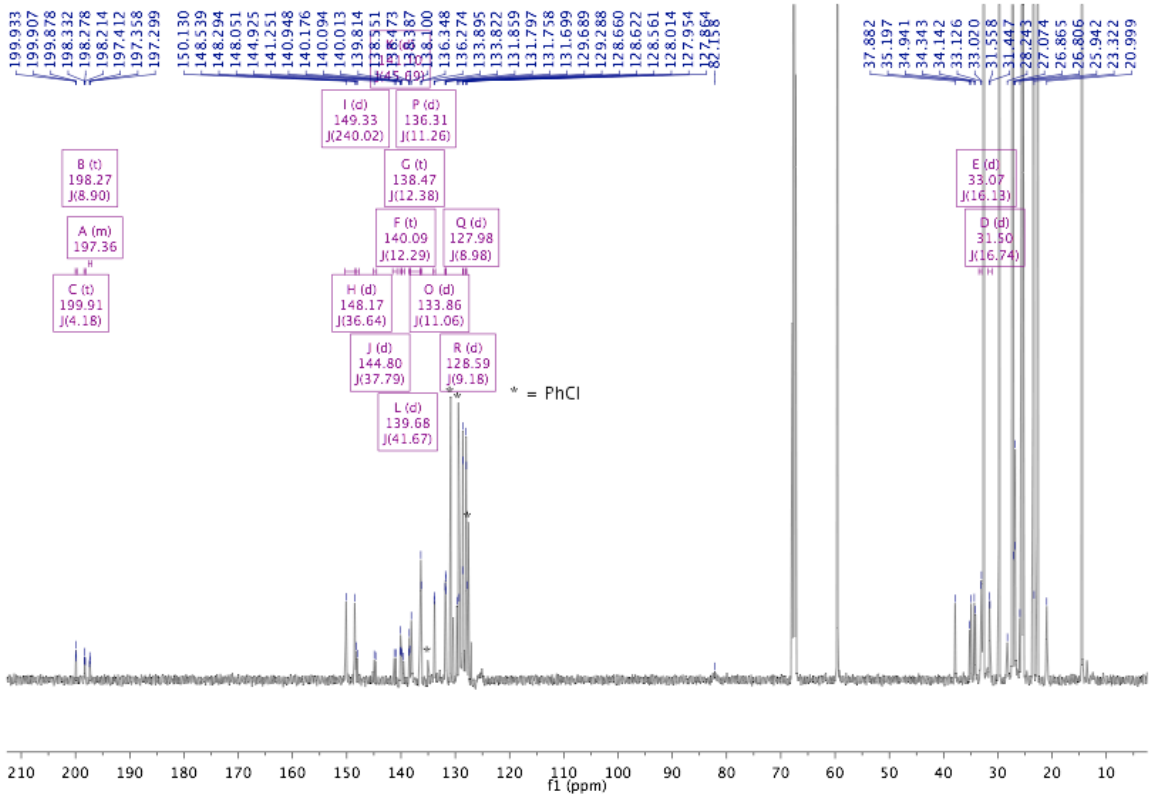


Figure S72. ^{13}C{^{1}H} NMR.

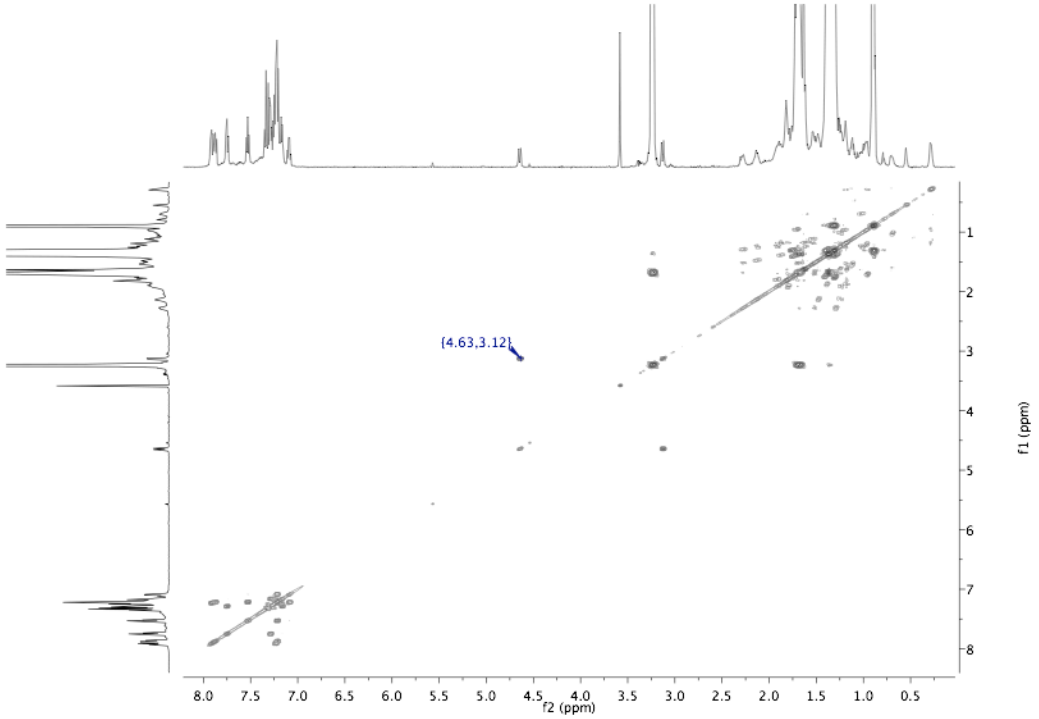


Figure S73. ^{1}H-^{1}H gCOSY. Correlation between Re-OC*H*$_2$-OBR$_3$ protons highlighted.

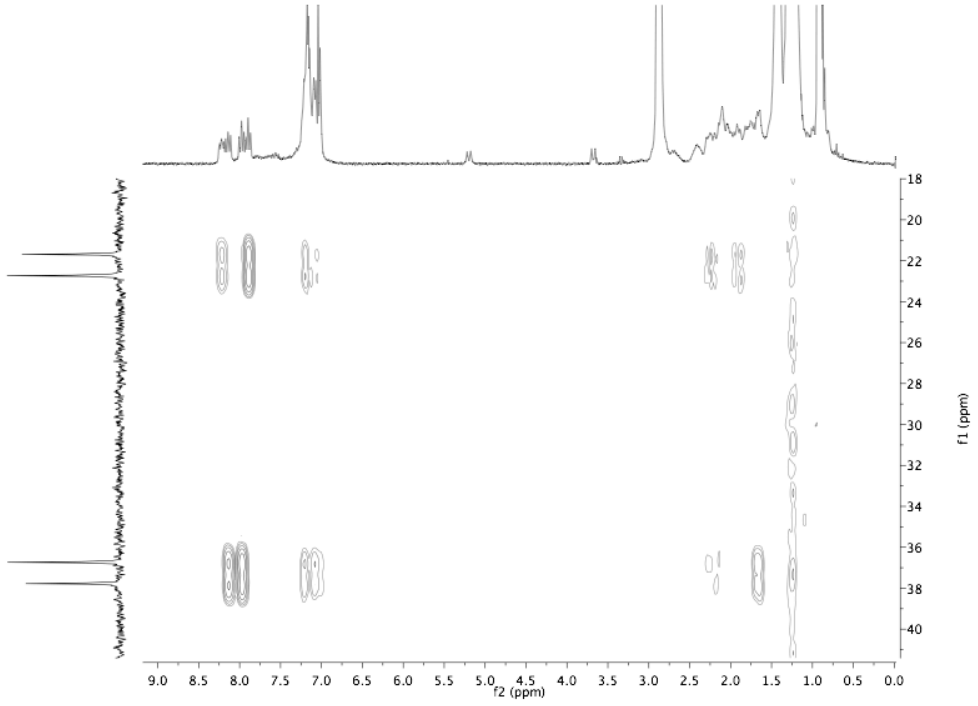


Figure S74. ^{1}H-^{31}P gHMBC (C_6D_5Cl). Note the lack of correlation between Re-OCH$_2$-BR$_3$ and phosphines.

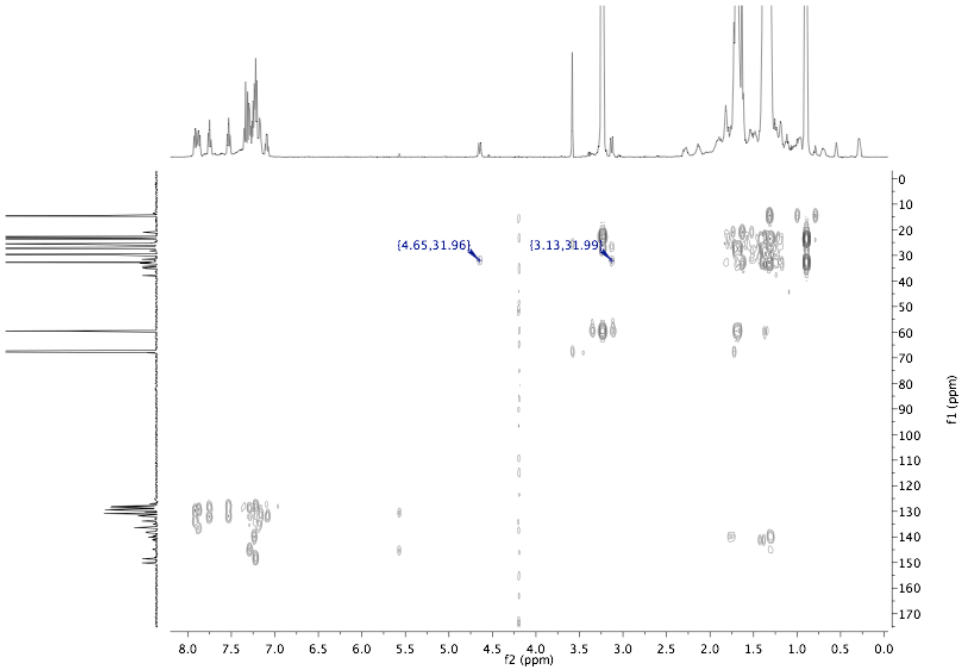


Figure S75. ^{1}H-^{13}C gHMBC. Correlation between Re-OCH_2-OBR$_3$ and Ph$_2$PCH$_2$B(C_8H_{14}) highlighted.

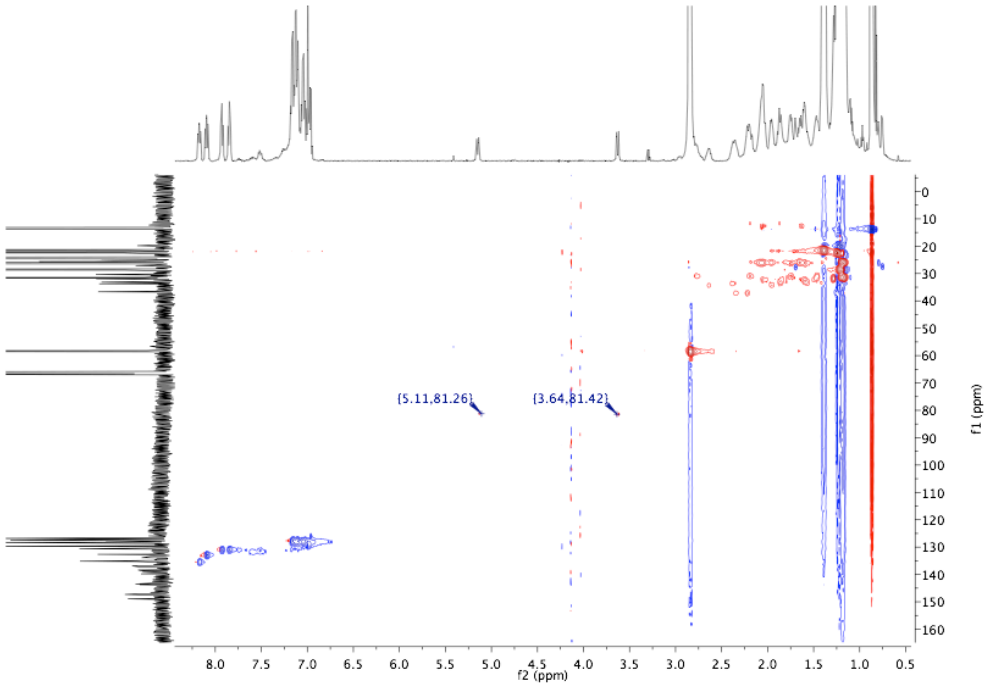


Figure S76. ^{1}H-^{13}C gHSQC (C_6D_5Cl). Correlation between Re-OCH_2BR$_3$ and Re-OCH$_2$BR$_3$ is highlighted.

Reaction of 2-M_2 with pyridine.

A vial was charged with 39.6 mg (0.0245 mmol) [**1-M_2**][$B(C_6F_5)_4$], 24.0 mg (0.0490 mmol) tetraheptylammonium tetrafluoroborate, and ~0.6 mL C_6D_5Cl. Solid [**HPt**][PF_6] (15.7 mg, 0.0245 mmol) was added in portions to the C_6D_5Cl solution with stirring, and the contents were added to a J-Young NMR tube. The tube was mixed by rotary motor overnight, at which point NMR spectroscopy showed clean conversion to boroxycarbene **2-M_2**. The NMR tube was returned to the glovebox, and the contents of the tube were poured onto an internal standard, 20 mg (0.0228 mmol) $(PPh_3)_2Re(CO)_3Br$. The mixture was filtered into a J-Young NMR tube, and NMR studies were carried out (there was no reaction or interaction with the Re-Br). Later, pyridine (6 μL, 0.0735, 3 equiv) was added. Instead of the expected B-O bond cleavage and downfield shift of the Re-CHO peak, a doublet at essentially unchanged chemical shift was observed. The ^{1}H NMR resonances sharpened and were consistent with two inequivalent ligands (two $Ph_2PCH_2BR_2$ groups). Two sharp ^{31}P NMR resonances were observed. Even with addition of a few drops (~100 equiv) pyridine, no significant spectral change was observed. Based on comparisons to the boroxycarbene spectra, the product is assigned as intramolecularly coordinated boroxycarbene with the second pendent borane binding pyridine. The spectral characteristics are quite similar to the low temperature spectra of **2-M_2** in the absence of pyridine, suggesting an analogous structure. **^{1}H NMR** (C_6D_5Cl, 300 MHz): δ 1.4-2.5 (br, m, $Ph_2PCH_2B(C_8H_{14})$), 1.83 (d, 13.7 Hz), 2.50 (d, 11.2 Hz), 6.9-7.1 (m, pyridine and Ph), 7.27 (br t, *J* = 7.01, pyridine), 7.39 (m, 6H, Ph), 7.58 (m, 6H), 8.61 (br, pyridine), 13.66 (d, J = 10.3 Hz, Re-C*H*O). **^{31}P{^{1}H} NMR** (C_6D_5Cl, 121 MHz): δ 2.56 (d, J_{PP} = 96.0 Hz, 1P), 7.41 (d, J_{PP} = 95.8 Hz, 1P).

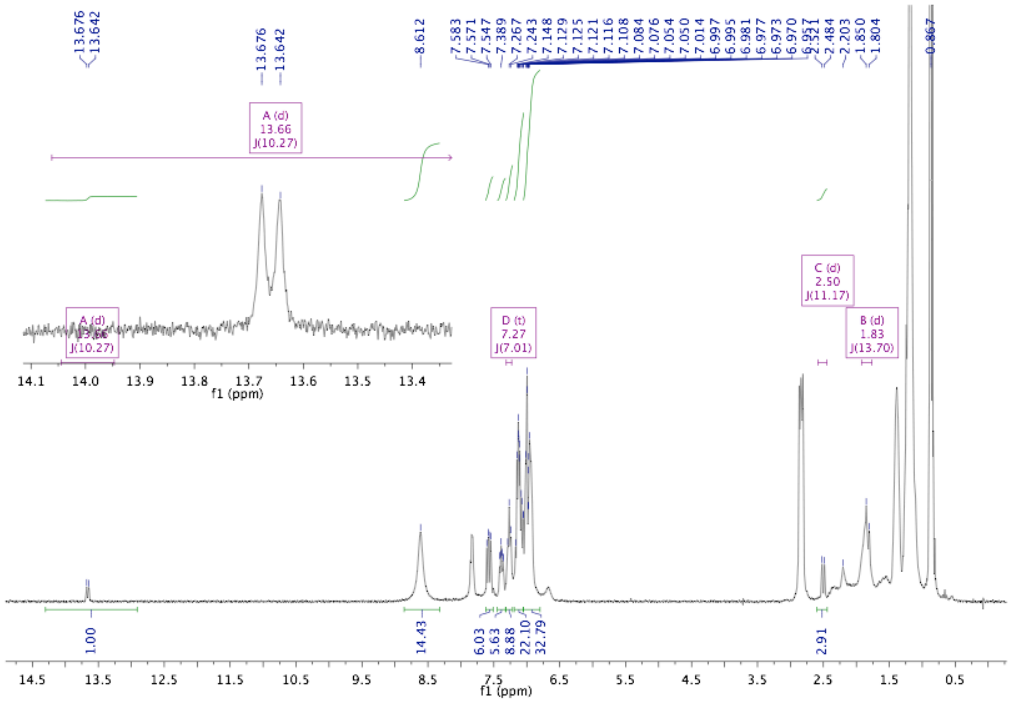


Figure S77. ^{1}H NMR.

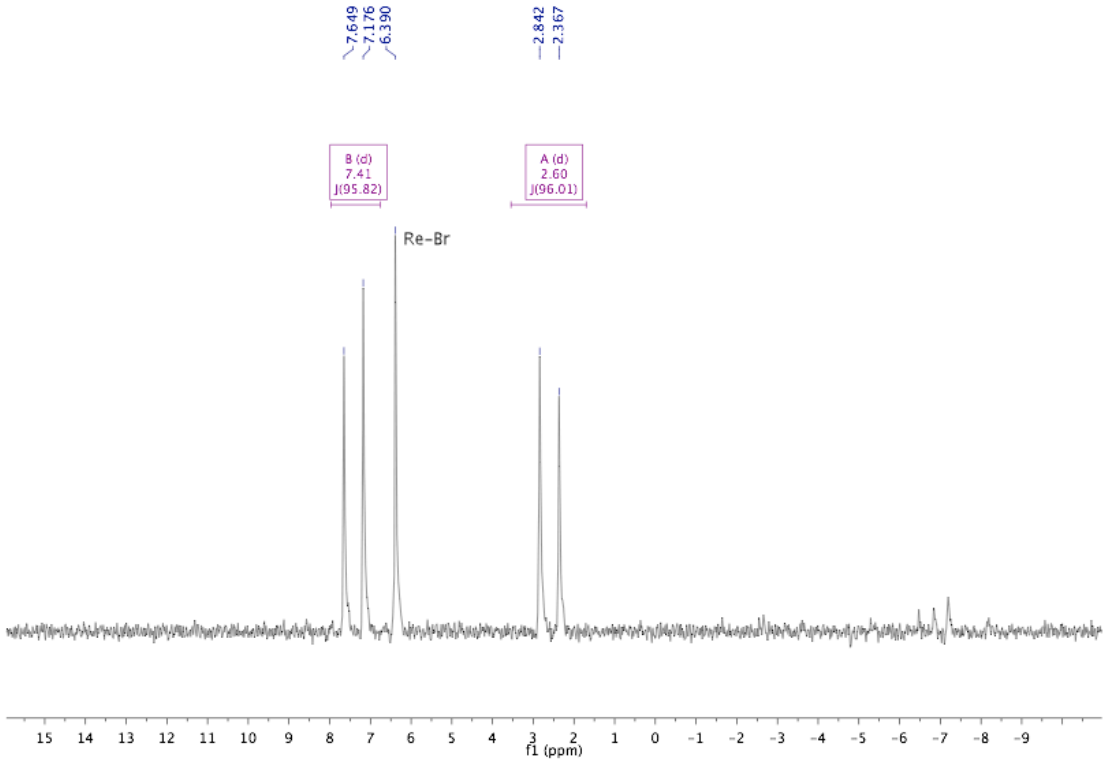


Figure S78. $^{31}P\{^{1}H\}$ NMR.

B. Pulsed Gradient Spin-Echo Diffusion NMR Studies on 2-E_2.

^{1}H NMR pulsed gradient spin-echo (PGSE) NMR measurements were performed using the standard echo pulse sequence on a Varian INOVA 500 MHz spectrometer at 298.15 K without spinning. The gradient shape was rectangular, with gradient length 2-4.2 ms, and the gradient strength was varied during the experiment. The spectra were processed with 2.0 Hz line broadening, and single exponential fits of selected resonances provided values for the diffusion coefficient D_t. The experimental diffusion coefficient was used to obtain values of hydrodynamic radii and volumes using Chen's modification[14] of the Stokes-Einstein equation:

$$D_t = \frac{kT}{c\pi\eta r_H}$$

$$c = \frac{6}{1 + 0.695\left(\frac{r_{\text{solv}}}{r_{\text{H}}}\right)^{2.234}} \qquad \text{(S1)}$$

$c = 6$ is the Stokes-Einstein equation.

The measurements were carried out in C_6D_5Cl (an atypical solvent for diffusion studies), due to low solubility of **2-E_2** in nonpolar solvents, reactivity with halogenated alkane solvents such as CD_2Cl_2, and interaction of the borane groups with strong donor solvents such as CD_3CN. The value for r_{solv} (2.69 x 10^{-10} m)[15] in equation S1 is that of C_6H_5Cl, a reasonably good approximation. The viscosity, η (0.008 Pa s^{-1})[16] is that of C_6D_5Cl. The classical Stokes-Einstein equation has c = 6, whereas the Chen modification corrects for molecules that are not much larger than the solvent they are in. As expected for a moderately sized organometallic molecule,

the experimental values of *c* were not 6, but varied from roughly 5.75-5.85. The molecules were assumed to be roughly spherical, and no further corrections were applied.

The PGSE NMR experiments were carried out in two phases, one with unknown aggregation, the other assumed to be strictly monomeric, and the size of the species compared. First, an NMR tube was charged with a C_6D_5Cl solution of **2-E$_2$** and $(PPh_3)_2Re(CO)_3Br$ (**6**) (internal standard of similar size and shape). The **2-E$_2$** solution was prepared either A) *in situ* (by treating [**1-E$_2$**][BF_4] with 1 equiv $NaHBEt_3$), or B) by dissolution of crudely isolated **2-E$_2$** (by precipitation of a C_6H_5Cl solution as prepared *in situ*, collection on a frit, and drying under vacuum). ^1H and $^{31}P\{^1H\}$ NMR experiments confirmed that **2-E$_2$** and **6** were the major species. A ^1H PGSE NMR experiment was carried out on this mixture, under which conditions the speciation of **2-E$_2$** was in question. After the first PGSE experiment was complete, the tube was returned to a nitrogen-filled glove box, and an excess of pyridine (3-12 equiv) was added by syringe, and the tube sealed. ^1H and $^{31}P\{^1H\}$ NMR experiments confirmed that **2-E$_2$** had been converted to the bis(pyridine) adduct **2-E$_2$**•(pyridine)$_2$, which has a significantly downfield-shifted formyl resonance, and a single ^{31}P resonance (see spectroscopic details elsewhere in the SI). There was no change in chemical shift or lineshape of **6** upon addition of pyridine, confirming that no interaction occurs with the internal standard. The excess pyridine appeared close to the expected shift of free pyridine in C_6D_5Cl,[17] indicating any exchange of bound and free pyridine must be slow on the NMR time-scale. A second ^1H PGSE NMR experiment was then carried out, and in these conditions the Re formyl was assumed to be strictly monomeric.

The data was processed as described above, providing D_t values for all species in the presence and absence of pyridine. Initial measurements provided a ratio of hydrodynamic volumes of **2-E$_2$**:**6**; then excess pyridine was added to the NMR tube, and the experiment was

repeated. If **2-E$_2$** were strictly monomeric in solution, the ratio would be expected to increase, since pyridine binding would increase the hydrodynamic volume; if **2-E$_2$** were strictly dimeric, the second ratio should be close to 0.5 times the first, as the monomer should have roughly half the hydrodynamic volume of the dimer. The values of the ratio were 2.34(7) before pyridine addition and 1.6(1) after; the decrease by a factor of 0.69(5) could reflect a monomer-dimer equilibrium, giving a time-averaged PGSE value.[18] Variable-temperature NMR experiments showed a subtle sharpening of the ^{1}H and ^{31}P resonances of **2-E$_2$** at low temperatures, but warming the solution led to decomposition, confounding complete analysis.

The uncertainty in the hydrodynamic volumes obtained from PGSE NMR experiments is significant; therefore no quantitative analysis was undertaken. The qualitative results are quite certain, however: the intermediate values for the speciation of **2-E$_2$** are reproducible under two different conditions (two runs of each experiment A and B) and are *inconsistent* with a strictly *monomeric solution structure* (in which case **2-E$_2$**•(pyridine)$_2$:**6** would be expected to be slightly *larger* than **2-E$_2$**:**6**). Furthermore, the observed reactivity of **2-E$_2$** is also consistent with a monomer-dimer equilibrium.

C. Reactivity Studies of 2-E$_2$.

Reaction of 2-E$_2$ with pyridine.

As part of a diffusion NMR experiment (see details of NMR experiment elsewhere in this SI), 26.0 mg (0.0247 mmol) [**1**][BF_4] was treated with 24.7 μL (0.0247 mmol) $NaHBEt_3$ (1.0 M in toluene) by syringe in ~0.6 mL C_6D_5Cl to form carbene **2-E$_2$**. 21.6 mg (0.0247 mmol) $(PPh_3)_2Re(CO)_3Br$ was added as an internal standard, and an NMR was taken. Roughly 45 minutes later, 6.0 μL (0.0741 mmol, 3 equiv) pyridine was added by syringe, and the reaction

was monitored by NMR. High initial conversion to one formyl product, **2-E_2•**(pyridine)$_2$, was observed, followed by slow decomposition to Re-H species over a few days. For **2-E_2•**(pyridine)$_2$: **^{1}H NMR** (C_6D_5Cl, 500 MHz): δ 0.48 (br m, 4H), 0.96 (br, 4H), 1.33 (6H), 1.57 (2H), 1.67 (4H), 1.8-2.0 (br m, 18H), 6.92 (pyridine), 7.20 (pyridine), 7.44 (m, 8H), 8.09 (pyridine), 15.21 (s, 1H, Re-C*H*O). **^{31}P{^{1}H} NMR** (C_6D_5Cl, 202 MHz): δ 11.8 (s).

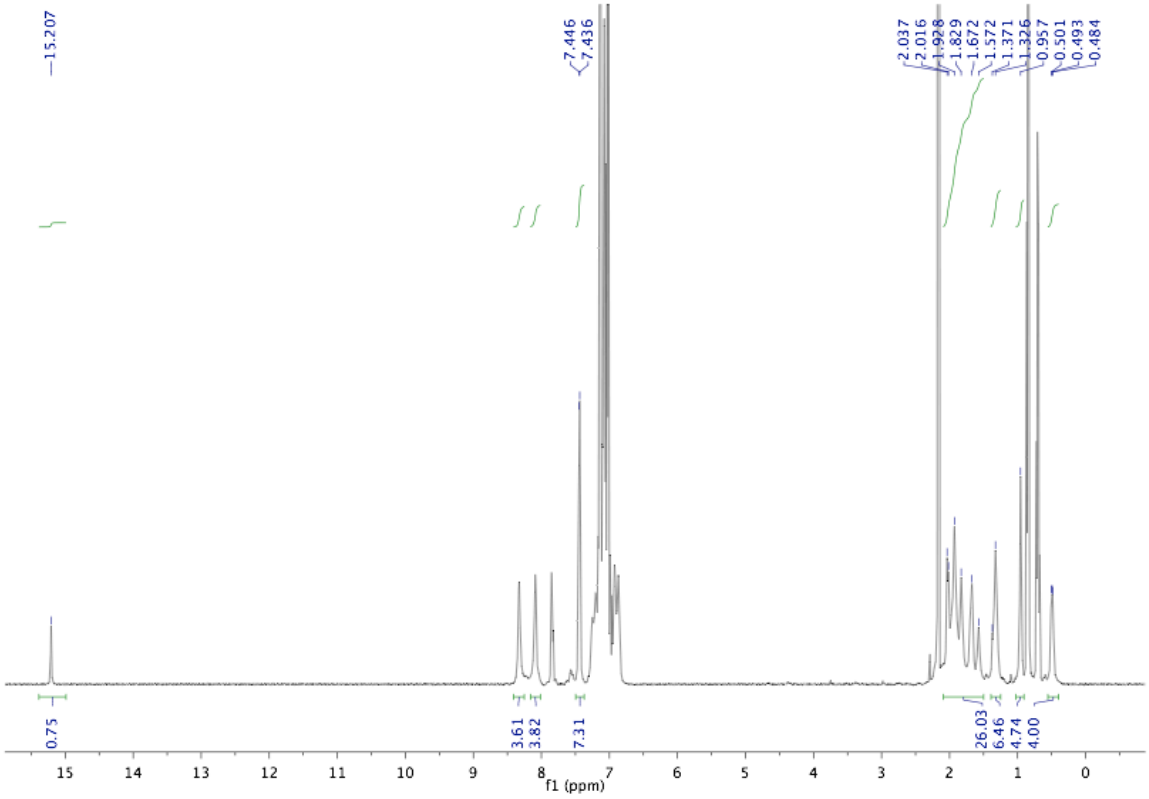


Figure S79. ^{1}H NMR.

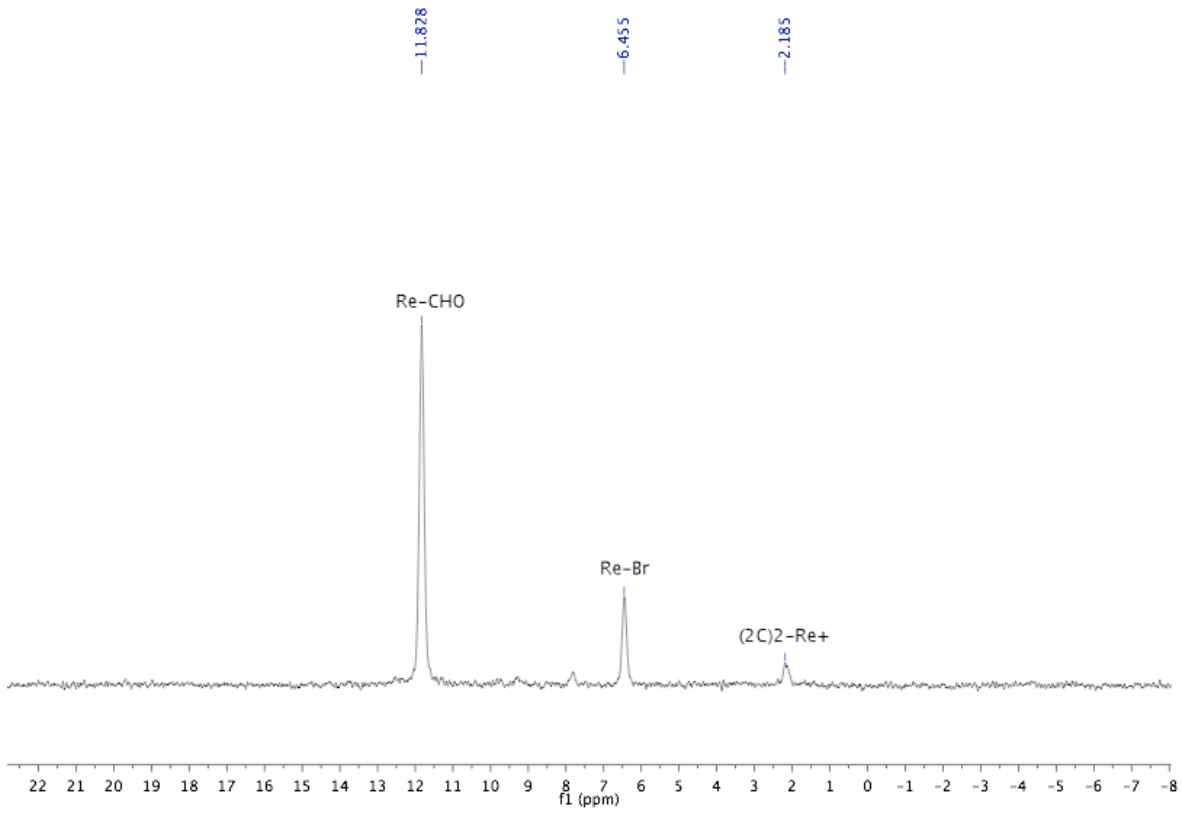


Figure S80. $^{31}P\{^{1}H\}$ NMR.

Thermolysis of 2-E_2.

A vial was charged with 53.2 mg (0.051 mmol) cation **[1-E_2]**[BF_4] and 0.5 mL C_6D_5Cl. 50.5 μL $NaHBEt_3$ (1.0 M in toluene) was added dropwise to afford carbene **2-E_2** as a pale yellow solution. The solution was transferred to a J-Young NMR tube and the carbene was formed quantitatively as assessed by NMR spectroscopy. The tube was submerged in a 90 °C oil bath for 30 minutes, after which time ^{1}H and $^{31}P\{^{1}H\}$ NMR showed ~80% conversion to a new species as a mixture with ~10% each [**1-E_2**]$^+$ and C-C coupled product [**3**]$^-$. The tube was brought into a glovebox, filtered, and the solvents removed under vacuum. The solids were extracted with benzene, filtered, and the solvents were removed, yielding 41 mg (0.042 mmol, 84%) ligand-activated product **7**, in ~90% purity. The product could be fully characterized by multinuclear

NMR studies, but the undesired product was not further purified. **^{1}H NMR** (C_6D_6, 500 MHz): δ 1.01-1.09 (m, 3H), 1.4-1.6 (m, 12H), 1.6-1.8 (m, 12H), 1.9-2.1 (m, 12H), 2.4-2.6 (m, 3H), 2.94 (m, 1H), 3.09 (m, 1H), 5.85 (br m, 1H), 6.9-7.1 (m, 12H), 7.75 (dt, J = 9.1, 17.9 Hz, 6H), 7.88 (t, J = 7.9 Hz, 2H). **^{31}P{^{1}H} NMR** (C_6D_6, 202 MHz): δ 12.6 (d, $^{2}J_{PP}$ = 124.8 Hz, 1P), 39.9 (d, $^{2}J_{PP}$ = 124.8 Hz, 1P). **^{13}C{^{1}H} NMR** (C_6D_6, 125 MHz): δ 22.2 (br, $Ph_2PCH_2CH_2B(C_8H_{14})$), 23.78, 24.33, 24.8 (br), 27.61 (d, $^{1}J_{PC}$ = 27.2 Hz, $Ph_2PCH_2CH_2B(C_8H_{14})$), 31.38 (d, $^{1}J_{PC}$ = 31.3 Hz, $Ph_2PCH_2CH_2CH(OBR_2)Re$), 31.93, 33.78, 33.84, 34.41, 34.64, 45.87 (dd, J_{PC} = 14.4, 5.3 Hz, $Ph_2PCH_2CH_2CH(OBR_2)Re$), 76.66 (dd, J_{PC} = 7.0, 2.2 Hz, $Ph_2PCH_2CH_2CH(OBR_2)Re$), 128.81 (d, $^{3}J_{PC}$ = 9.3 Hz, *m*-Ph), 128.90 (d, $^{3}J_{PC}$ = 9.3 Hz, *m*-Ph), 129.08 (d, $^{3}J_{PC}$ = 9.7 Hz, *m*-Ph), 129.12 (d, $^{3}J_{PC}$ = 9.5 Hz, *m*-Ph), 129.93 (d, $^{4}J_{PC}$ = 1.8 Hz, *p*-Ph), 130.17 (d, $^{4}J_{PC}$ = 1.9 Hz, *p*-Ph), 130.25 (d, $^{4}J_{PC}$ = 1.9 Hz, *p*-Ph), 130.32 (d, $^{4}J_{PC}$ = 2 Hz, *p*-Ph), 132.07 (d, $^{2}J_{PC}$ = 10.5 Hz, *o*-Ph), 132.67 (d, $^{2}J_{PC}$ = 11.0 Hz, *o*-Ph), 132.68 (d, $^{2}J_{PC}$ = 10.2 Hz, *o*-Ph), 133.99 (d, $^{2}J_{PC}$ = 9.9 Hz, *o*-Ph), 137.37 (d, $^{1}J_{PC}$ = 43.6 Hz, *ipso*-Ph), 137.71 (d, $^{1}J_{PC}$ = 45.7 Hz, *ipso*-Ph), 137.90 (d, $^{1}J_{PC}$ = 44.5 Hz, *ipso*-Ph), 139.54 (d, $^{1}J_{PC}$ = 42.2 Hz, *ipso*-Ph), 195.17 (t, $^{2}J_{PC}$ = 9.3 Hz, Re-*C*O), 198.65 (t, $^{2}J_{PC}$ = 5.7 Hz, Re-*C*O), 199.12 (t, $^{2}J_{PC}$ = 9.4 Hz, Re-*C*O). **^{11}B{^{1}H} NMR** (C_6D_6, 160 MHz): δ 54.9, 88.0. Assignments were made using ^{1}H-^{31}P gHMBC, ^{1}H-^{13}C gHMQC, ^{1}H-^{13}C gHMBC, and ^{1}H-^{1}H gCOSY 2-D NMR experiments.

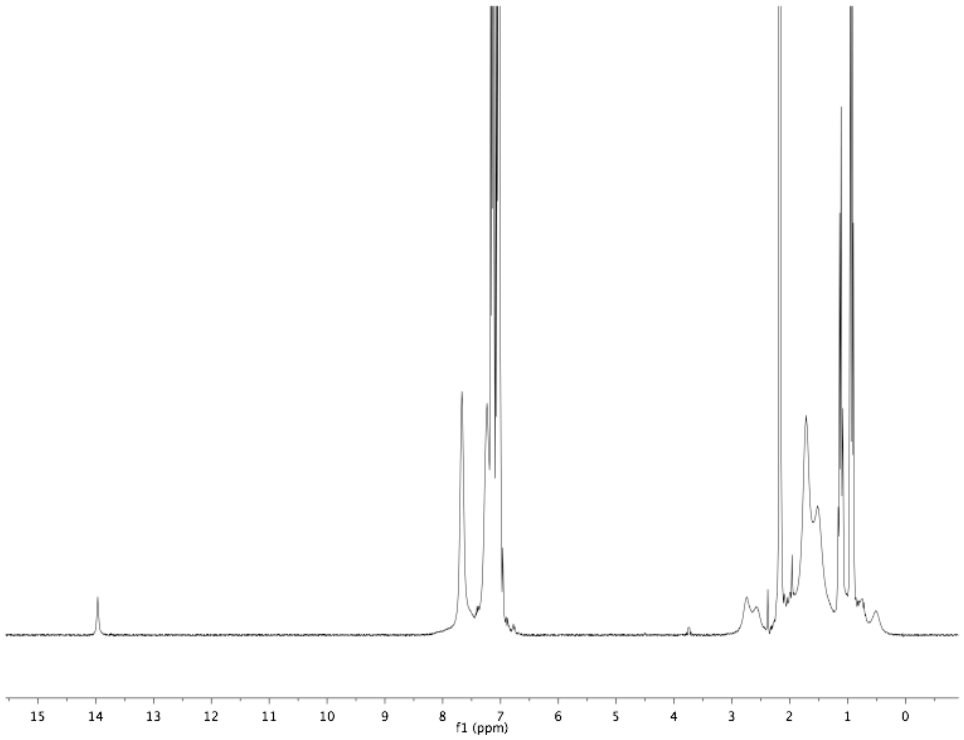


Figure S81. ^{1}H NMR of in-situ generated carbene.

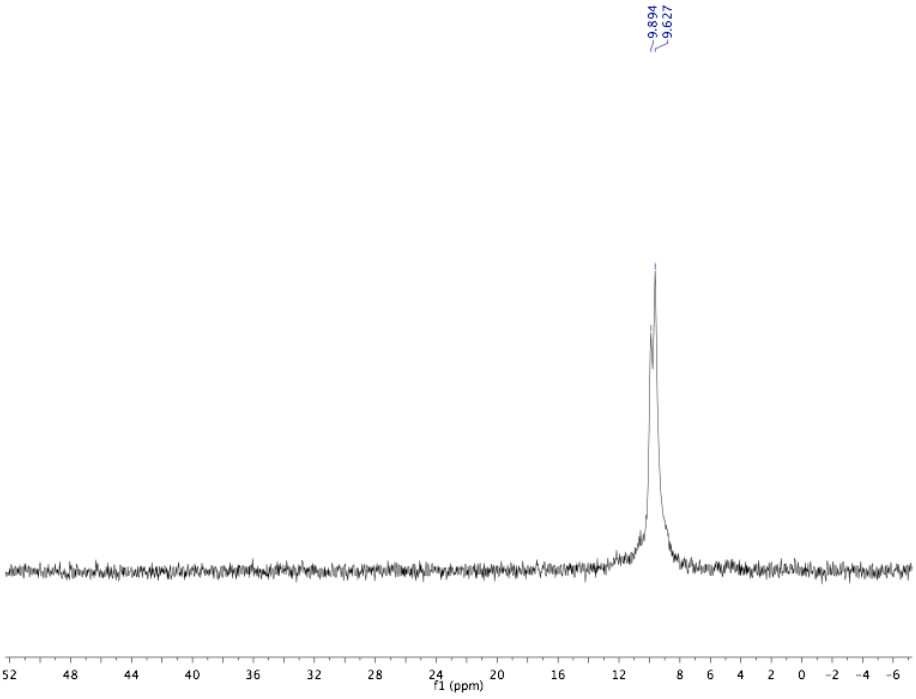


Figure S82. $^{31}P\{^{1}H\}$ NMR of in-situ generated carbene.

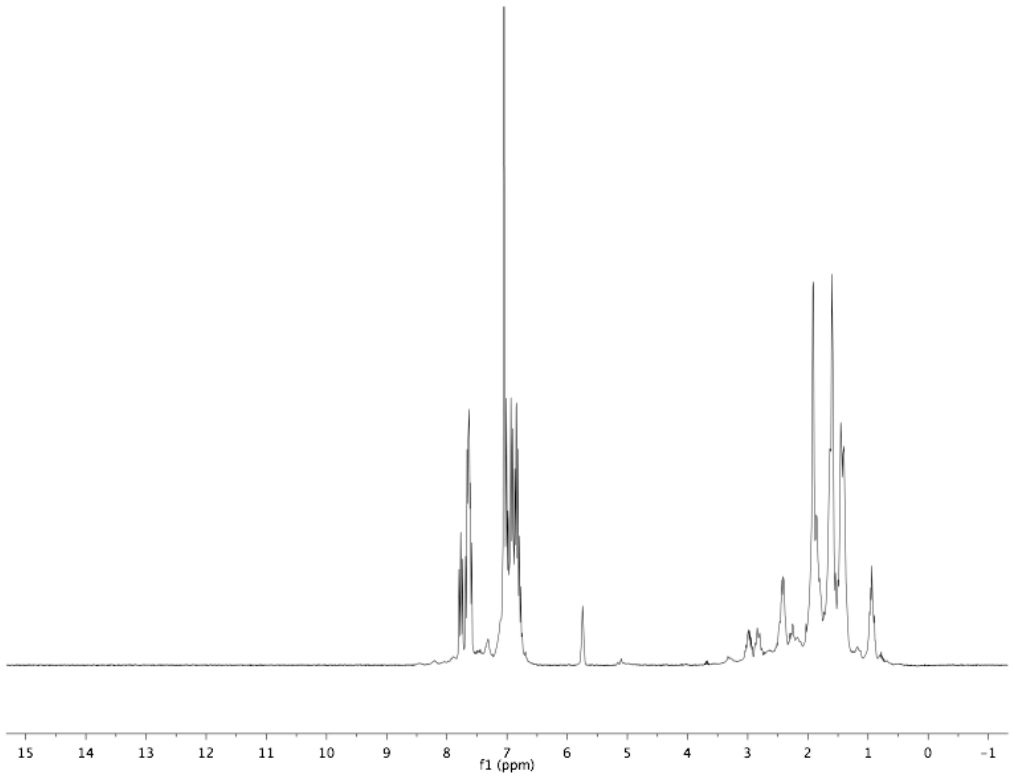


Figure S83. ^{1}H NMR after thermolysis and workup.

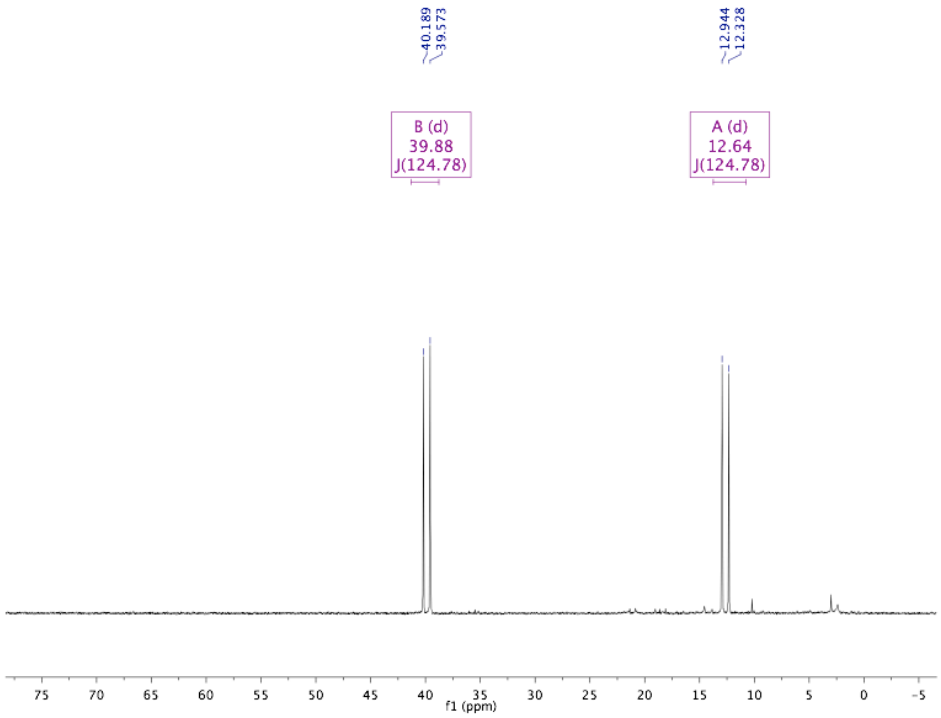


Figure S84. $^{31}P\{^{1}H\}$ NMR.

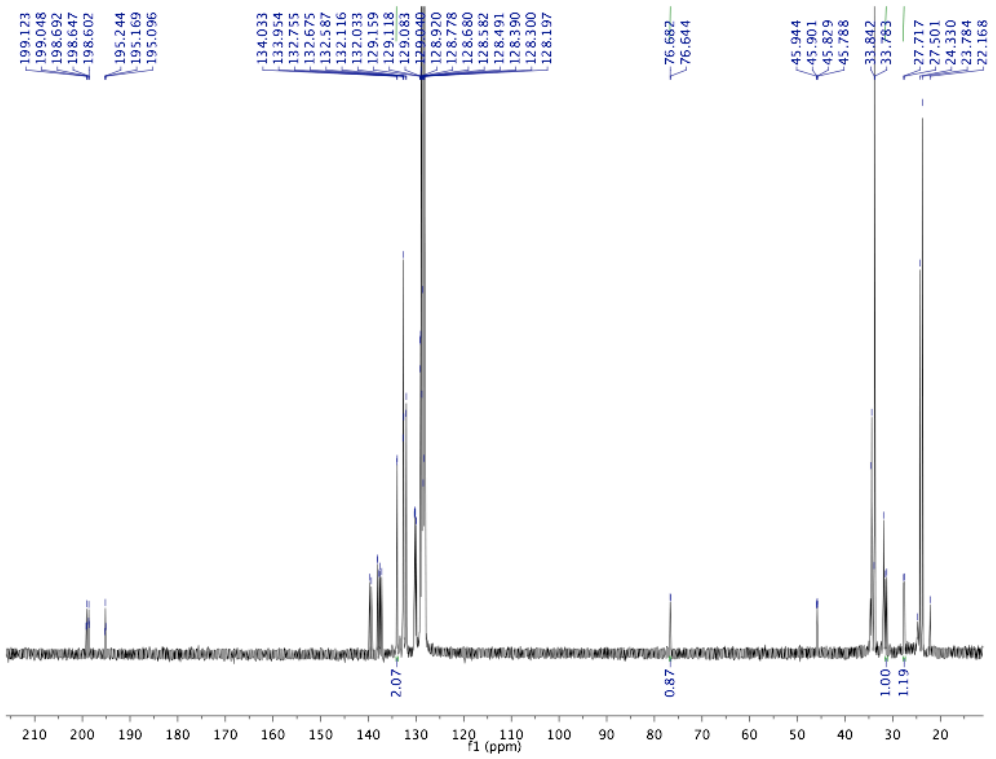


Figure S85. $^{13}C\{^{1}H\}$ NMR.

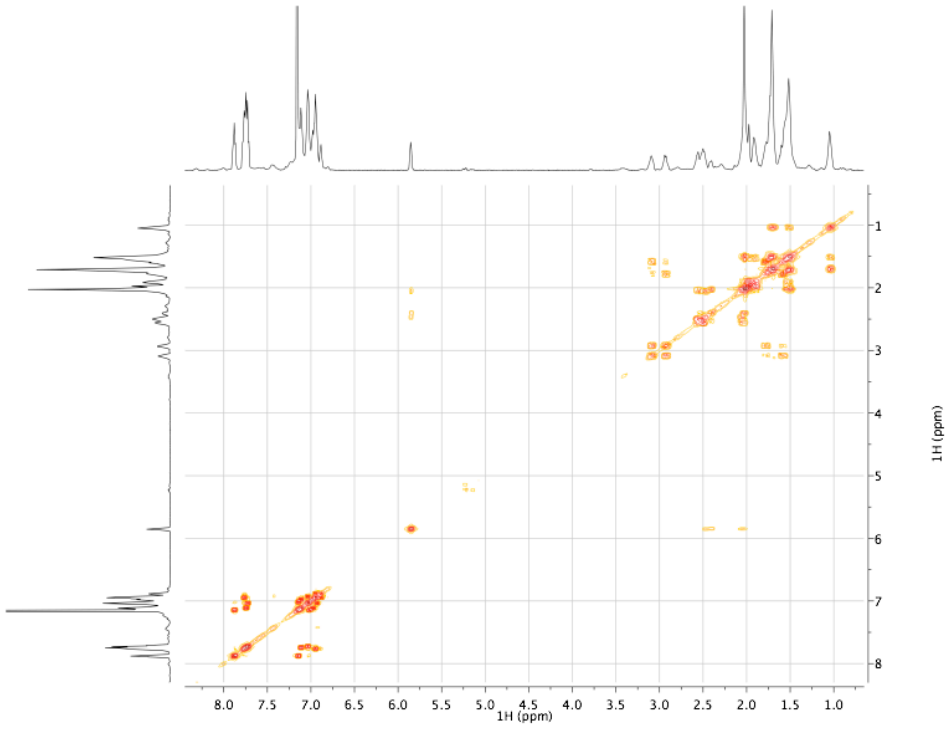


Figure S86. ^{1}H-^{1}H gCOSY.

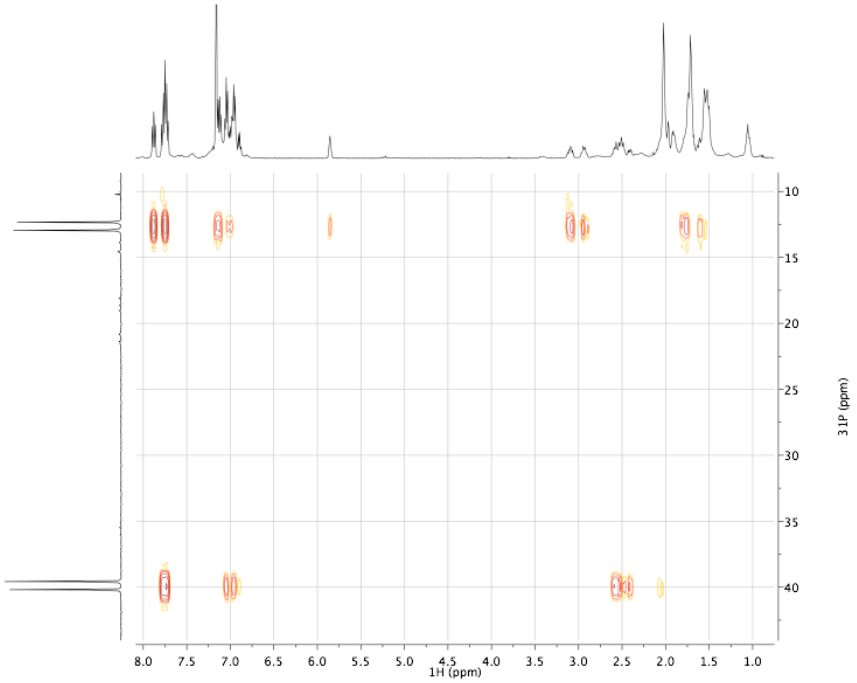


Figure S87. ^{1}H-^{31}P gHMBC.

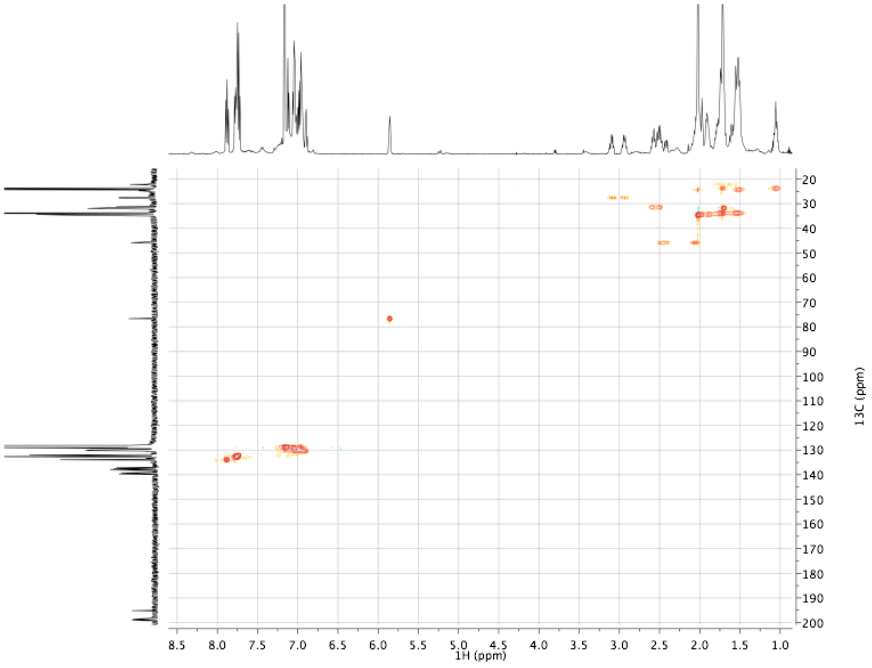


Figure S88. ^{1}H-^{13}C gHMQC.

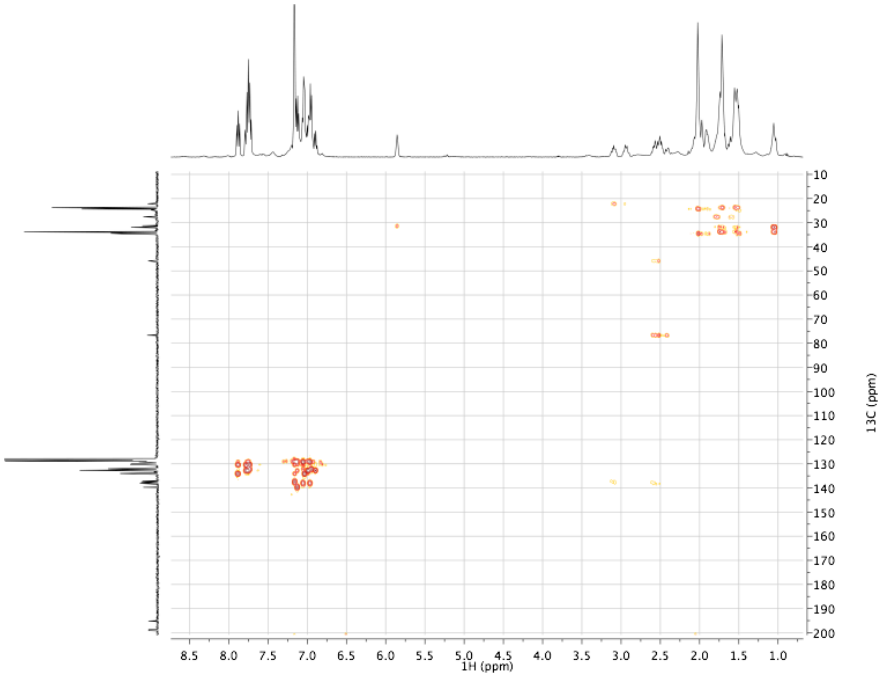


Figure S89. ^{1}H-^{13}C gHMBC.

Reaction of 2-E_2 with H_2O.

Carbene **2-E_2** was prepared in the usual manner by dropwise addition of 21.8 μL (0.0218 mmol) $NaHBEt_3$ (1.0 M in toluene) to a rapidly stirring C_6D_5Cl solution of 23.0 mg (0.0218 mmol) cation [**1-E_2**]$^+$. ^{1}H and $^{31}P\{^{1}H\}$ NMR studies showed clean formation of the carbene. 30 minutes after preparation, 0.4 μL (0.0218 mmol) degassed deionized H_2O was added by syringe. After addition, the solution immediately began bubbling, the yellow color of the carbene bleached, and some precipitates formed. A $^{31}P\{^{1}H\}$ NMR experiment showed one prominent singlet at δ 1.4, in a similar location as the cation [**1-E_2**]$^+$ (δ 0.3), along with minor impurities. The ^{1}H NMR spectrum showed complete consumption of the carbene resonance at δ 13.96, and a conspicuous resonance for H_2 gas at δ 4.49. The rest of the spectrum was rather broad and non-descript, but matched the spectrum of crystals of **8** obtained from a separate reaction of carbene **2-E_2** with wet CO.

Reaction of 2-E_2 with [Me_3NH][BPh_4].

Carbene **2-E_2** was prepared in the usual manner by dropwise addition of 21.2 μL (0.0212 mmol) $NaHBEt_3$ (1.0 M in toluene) to a rapidly stirring C_6D_5Cl solution of 22.3 mg (0.0212 mmol) [**1-E_2**][BF_4]. After stirring for 3 minutes, the mixture was added to a J-Young NMR tube already charged with 8.0 mg (0.0212 mmol) [Me_3NH][BPh_4]. Although the acid is not very soluble, and some solids remained at the bottom of the tube, the yellow color of the carbene disappeared and bubbles were observed. The single $^{31}P\{^1H\}$ NMR signal at δ 0.5 (s) and ^1H NMR pattern is indicative of a symmetric cationic bisphosphine tetracarbonyl species. Although a small amount of carbene remained after 30 minutes, no remaining carbene was detected 24 hours later. Hydrogen was observed in the ^1H NMR spectrum.

Reaction of 2-E_2 with [^{t}Bu_3PH][$HB(C_6F_5)_4$].

Boroxycarbene **2-E_2** was prepared in the usual manner by dropwise addition of 17.3 μL (0.0173 mmol) $NaHBEt_3$ (1.0 M in toluene) to a rapidly stirring C_6D_5Cl solution of 18.2 mg (0.0173 mmol) [**1-E_2**][BF_4]. After stirring for 3 minutes, the mixture was added to a J-Young NMR tube already charged with 12.4 mg (0.0173 mmol) [^{t}Bu_3PH][$HB(C_6F_5)_4$]. The tube was sealed and shaken, and bubbles immediately started forming, along with a bleach of the yellow color of the carbene. A ^1H NMR experiment showed a peak for H_2 gas at δ 4.49, and aryl and $Ph_2PCH_2CH_2B(C_8H_{14})$ resonances at similar – but slightly different—chemical shifts from [**1-E_2**][BF_4]. A very broad peak near δ 4 is consistent with a BH functionality, and the presence of [$HB(C_6F_5)_3$] was further confirmed by ^{19}F NMR, δ -133.0, -164.3, -167.0. A $^{31}P\{^1H\}$ NMR experiment showed two singlets: free P^tBu_3 at δ 62.1 and a rhenium species at δ 0.3, in the same

location as [**1-E$_2$**][BF_4]. Thus we assign the product as closely related to cation **1**, [$(Ph_2P(CH_2)_2B(C_8H_{14}))_2Re(CO)_4$][$HB(C_6F_5)_4$]. Heating at 50 °C for one week resulted in no discernable reaction. Elevated temperatures (135 °C) led to decomposition of the ligands, including the presence of cyclooctene.

NMR-scale reaction of [Na][3-E$_2$] with [Pt][BAr$^F{}_4$]$_2$.

To a ~0.6 mL THF-d_8 solution of 21.0 mg (0.0199 mmol) [**1-E$_2$**][BF_4] was added 39.9 μL (0.0399 mmol, 2 equiv) $NaHBEt_3$ (1.0 M in toluene) dropwise with stirring. The mixture was filtered into a J-Young NMR tube, and NMR spectroscopy showed clean formation of [**3-E$_2$**]$^-$. The tube was returned to the glove box, and the contents poured onto 88.6 mg (0.0199 mmol) [**Pt**][BAr$^F{}_4$]$_2$, which was dissolved and the reaction mixture returned to the tube. NMR spectroscopic monitoring revealed no detectable reaction of [**3-E$_2$**]$^-$ or formation of [**HPt**]$^+$ over 24 hours.

Reaction of [Na][3-E$_2$] with MeOTf.

To a 5 mL toluene suspension of 35.8 mg (0.0341 mmol) [Na]**[3-E$_2$]** was added 3.9 μL (0.0341 mmol) MeOTf by syringe, with stirring. The reaction mixture was stirred 30 minutes, filtered, washing with 0.5 mL toluene and 1 mL pentane, affording clear yellow filtrate (white solids left on filter). The solvents were removed under vacuum, giving 27 mg (80%) yield of yellow product. **^{1}H NMR** (THF-d_8, 300 MHz) showed a characteristic pair of doublets at 3.97 (d, J_{HH} = 18.8 Hz) and 4.61 (d, J_{HH} = 18.8 Hz), along with a singlet at 3.18 (3H) for the new methyl group. Integration of the crowded alkyl and aryl regions was not satisfactory, however. **^{31}P NMR** (THF-d_8, 300 MHz) showed only one product, 5.5 (d, J_{PP} = 110.2 Hz) and 14.1 (d, J_{PP} = 109.7 Hz).

Crystallographic characterization, which would determine which oxygen was methylated, has been thus far elusive, and the material was not further purified or characterized.

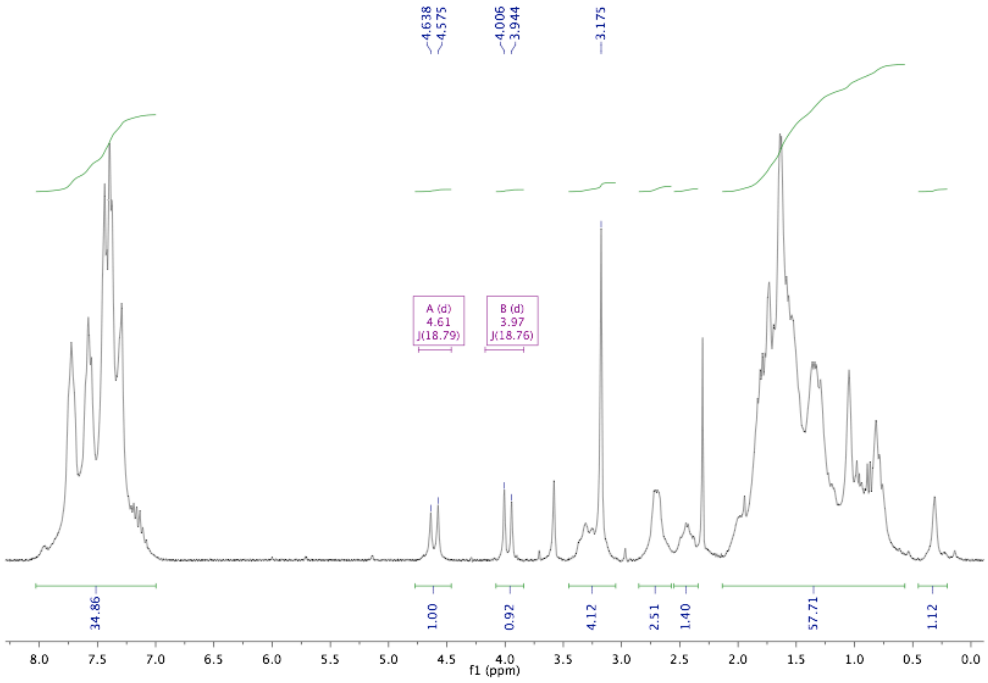


Figure S90. ^{1}H NMR.

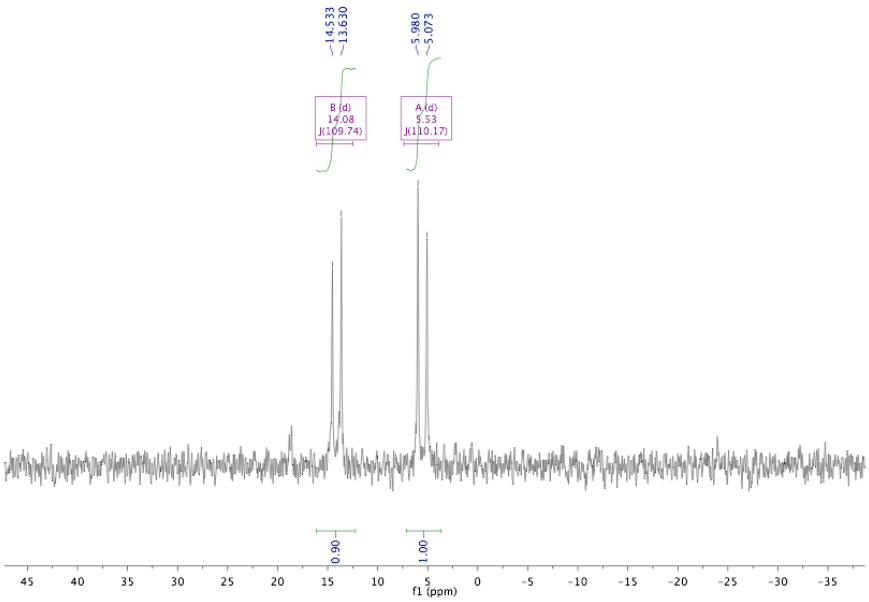


Figure S91. ^{31}P{^{1}H} NMR.

D. Mechanism Studies on the Reduction of $[\mathbf{1\text{-}E_2}]^+$.

Reaction of $[\mathbf{1\text{-}E_2}][BF_4]$ with $[\mathbf{HPt}][PF_6]$ at -40 °C.

A J-Young NMR tube was charged with a ~0.2 mL C_6D_5Cl solution of 22.4 mg (0.0213 mmol) $[\mathbf{1\text{-}E_2}][BF_4]$. The solution was frozen in a liquid nitrogen cooled cold well in the glove box. A ~0.1 mL layer of C_6D_5Cl was added, and the tube was cooled to freeze the solvents again. Finally, a layer of ~0.3 mL C_6D_5Cl solution of 13.6 mg (0.0213 mmol) $[\mathbf{HPt}][PF_6]$ was added, and the solution frozen. The tube was sealed, removed from the glove box, and inserted into a dry ice / acetone bath to keep the contents of the tube frozen. Meanwhile, the NMR probe was cooled to -40 °C. The tube was allowed to just start to thaw, at which point it was shaken vigorously for a few seconds, and then inserted into the -40 °C probe. NMR spectra were obtained at various times and temperatures, with the temperature slowly being raised to 0 °C, at which point the reaction was complete. In separate experiments a broad ^{31}P signal at -5.9, slightly downfield of $[\mathbf{HPt}][PF_6]$ (δ -7.2) was always observed (sometimes an additional sharp peak for $[\mathbf{HPt}][PF_6]$ was observed), appearing to be an intermediate of hydride transfer from Pt to $[\mathbf{1\text{-}E_2}]^+$. A set of two doublets at δ 1.15 (J_{PP} = 71 Hz) and δ 4.5 (J_{PP} = 75 Hz) were also observed, which disappeared at roughly the same rate as the broad hydride signal.

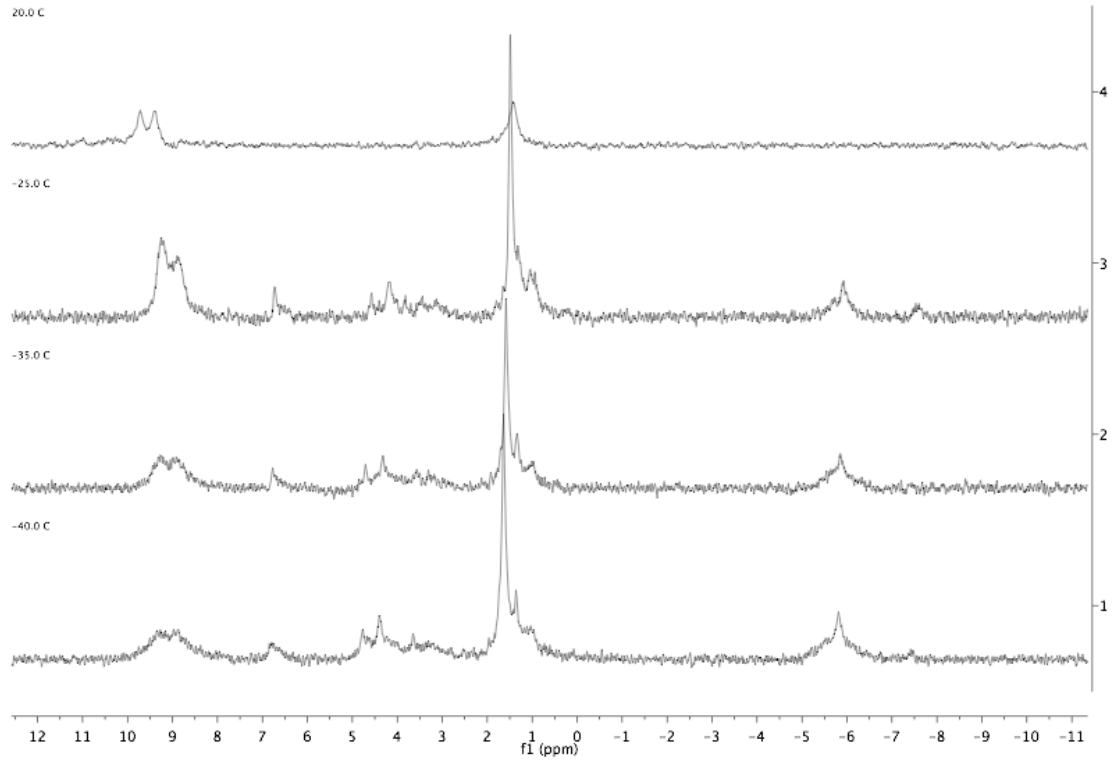


Figure S92. $^{31}P\{^{1}H\}$ NMR as temperature is raised.

Reaction of [1-E_2][BF_4] with 2 equiv $NaHBEt_3$ in C_6D_5Cl at – 40 °C.

Boroxycarbene **2-E_2** was formed by dropwise addition of 28.4 μL (0.0284 mmol) $NaHBEt_3$ (1.0 M in toluene) to a rapidly stirring ~0.6 mL C_6D_5Cl solution of 29.9 mg (0.0284 mmol) [**1-E_2**][BF_4]. 1H and ^{31}P NMR spectroscopy after formation of **2-E_2** showed essentially quantitative conversion to the desired boroxycarbene. The NMR tube (J-Young) was returned to the glove box, and placed in a liquid nitrogen cooled well to freeze the contents. A small amount (~100 μL) of C_6D_5Cl was layered on top, and the contents were frozen again. Finally, 28.4 μL (0.0284 mmol) $NaHBEt_3$ (1.0 M in toluene) was added to the tube, and the contents were frozen. The tube was sealed and removed from the box, and inserted into a dry ice / acetone bath to keep the contents frozen. Meanwhile, the NMR spectrometer probe was cooled to – 40 °C. The tube was

removed from the cold bath and allowed to just start to thaw, at which point the tube was shaken vigorously, and re-frozen. The tube was then inserted into the pre-cooled (– 40 °C) probe while still frozen, and was allowed to thaw in the probe. Upon thawing, a single Re-containing species was observed by multinuclear NMR experiments, characterized spectroscopically as the anionic bis-boroxycarbene species [**9**]$^-$. The species was quite stable at – 40 °C, but as the probe was warmed to 0 °C the intensity of the signals of [**9**]$^-$ steadily decreased until no Re-containing products were present in solution. Ejecting the NMR tube showed large amounts of pale yellow precipitates; extraction with THF-d_8 proved these solids to be the ultimate double-reduction product [**3-E$_2$**]$^-$. Spectroscopic characterization of [**9**]$^-$: **^{1}H NMR** (C_6D_5Cl, 500 MHz, – 40 °C, all peaks were broad): δ -0.15 (4H), 0.39 (4H), 0.66 (2H), 1.42 (2H), 1.57 (4H), 1.73 (16H), 1.98 (2H), 2.34 (2H), 2.64 (4H), 3.07 (4H), 7.58 (10H), 7.62 (10H), 16.43 (2H). **^{31}P{^{1}H} NMR** (C_6D_5Cl, 202 MHz, – 40 °C): δ 10.0 (s). **^{13}C{^{1}H} NMR** (C_6D_5Cl, 126 MHz, – 40 °C): δ 13.35 (br), 25.57, 26.02, 28.02 (br), 30.29, 38.23, 39.71, 130.79, 132.11, 142.82 (br m; other aromatic peaks are obscured by toluene and C_6D_5Cl peaks), 198.31 (m, Re-*C*O), 291.57 (Re-*C*HO).

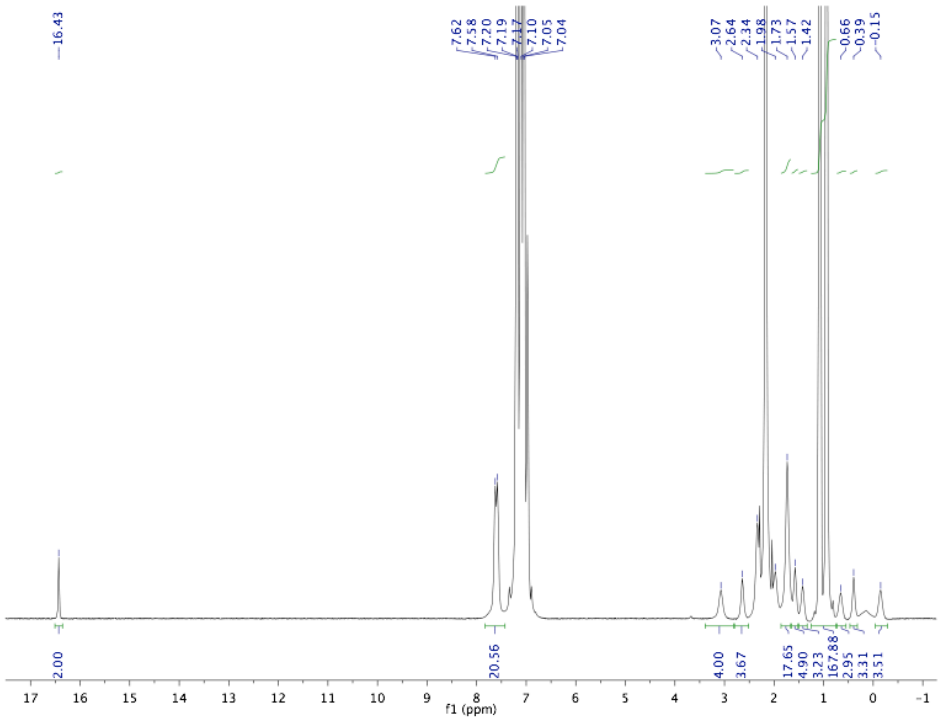


Figure S93. ^{1}H NMR.

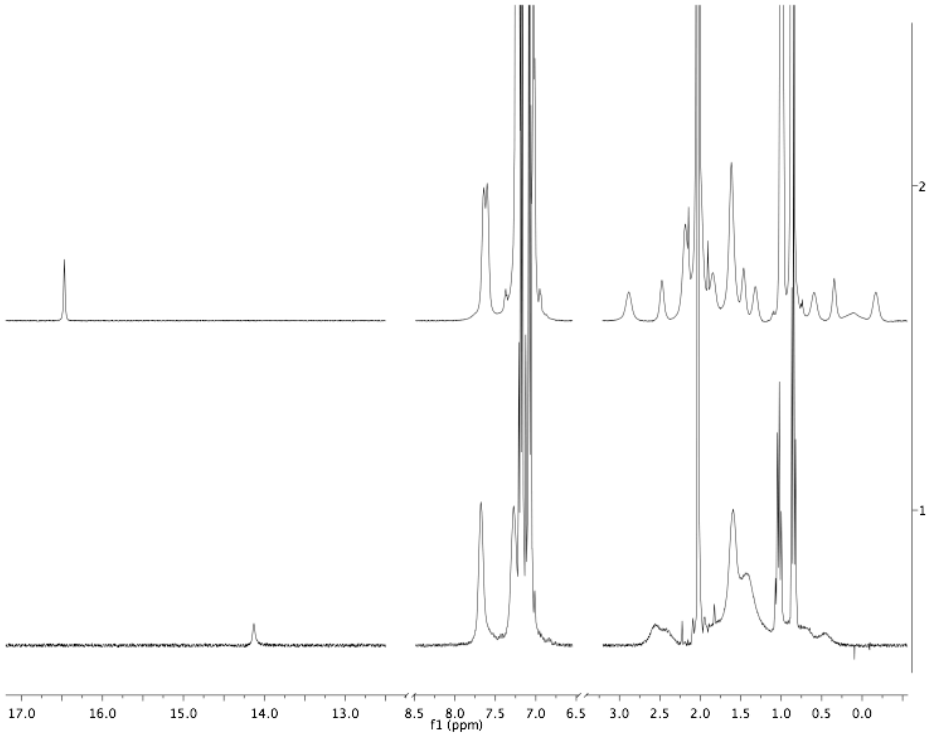


Figure S94. ^{1}H NMR overlay after first (bottom) and second (top) hydride addition.

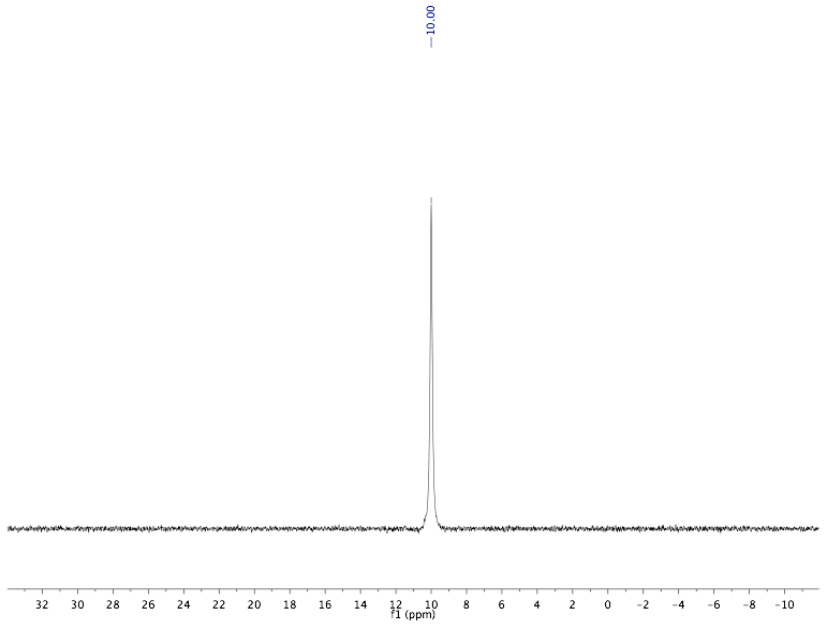


Figure S95. $^{31}P\{^{1}H\}$ NMR.

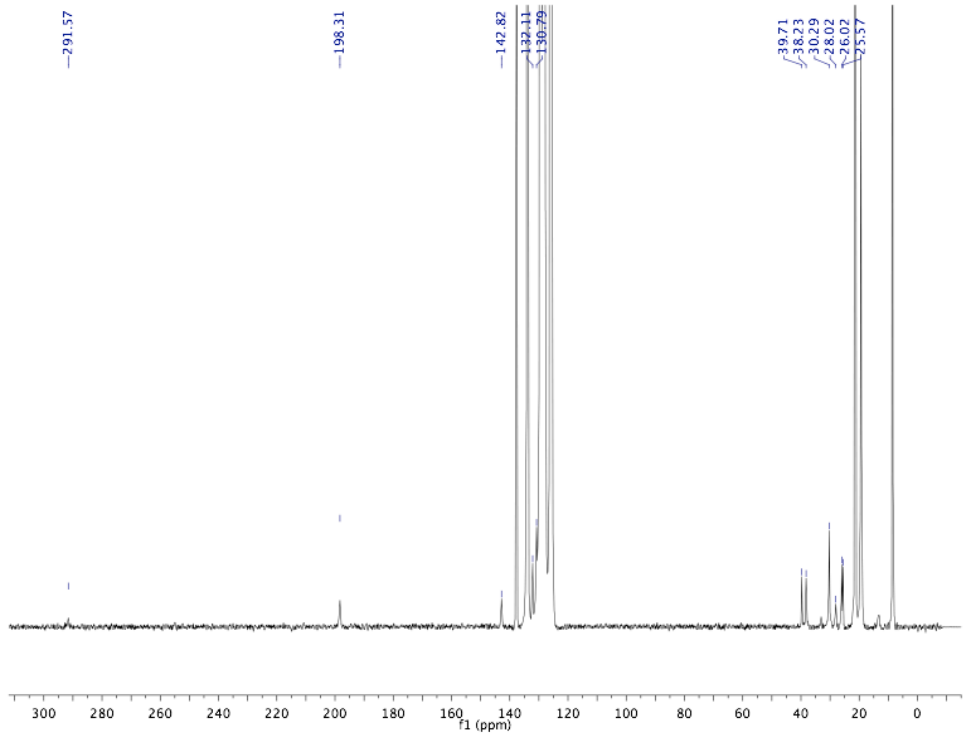


Figure S96. $^{13}C\{^{1}H\}$ NMR.

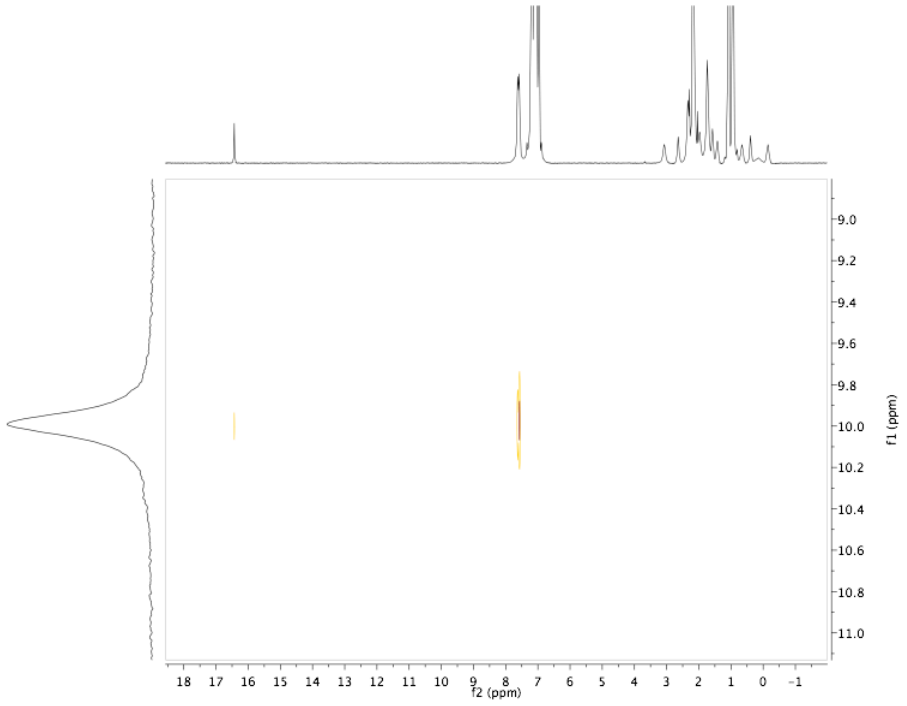


Figure S97. ^{1}H-^{31}P gHMBC.

Reaction of [HPt(dmpe)$_2$][PF$_6$] with BEt$_3$.

A J-Young NMR tube was charged with 23.5 mg (0.0366 mol) [**HPt**][PF$_6$] and ~0.6 mL C_6D_5Cl. 36.6 μL (0.0366 mmol) BEt_3 (1.0 M in hexanes) was added by syringe, which prompted some precipitation. The tube was removed from the box and variable temperature NMR experiments were undertaken, showing dynamic fluxional spectra that changed with temperature. At room temperature only a broad signal for [**HPt**]$^+$ was observed in the ^{1}H NMR spectrum at -11.7. Upon cooling to -40 °C that signal sharpened into a pentet and an additional broad doublet at -3.23 (J_{PH} = 165 Hz, J_{PtH} = 952 Hz) was observed. The latter signal is consistent with a bridging Pt-H-B species. Similar results were obtained when $Ph_2PCH_2CH_2B(C_8H_{14})$ was used in place of BEt_3. The $^{31}P\{^{1}H\}$ NMR showed broad signals at -7.3 and -2.4. Cooling to -40 °C led to sharpening of the signals: -7.3 (J_{PtP} = 2230 Hz) and -1.6 (slightly broadened, no Pt coupling observed).

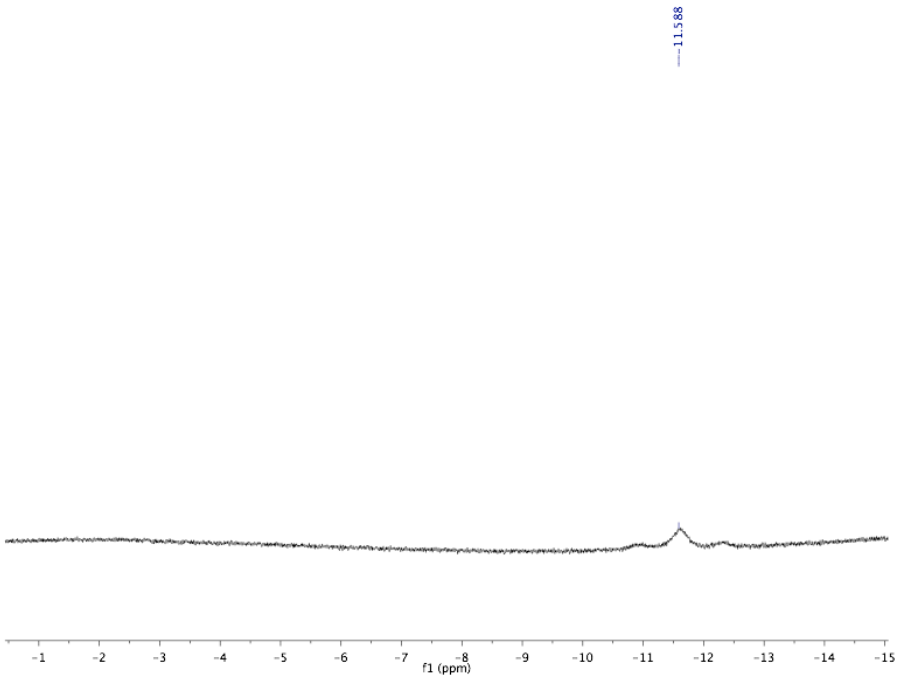


Figure S98. ^{1}H NMR (20 °C), hydride region.

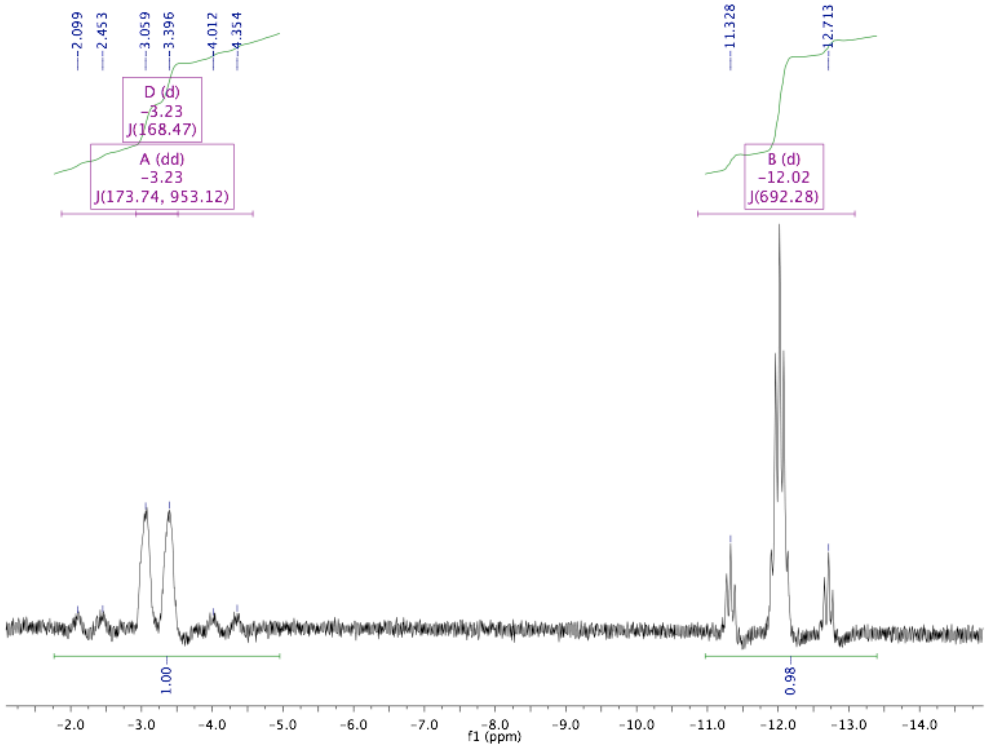


Figure S99. ^{1}H NMR (-40 °C), hydride region.

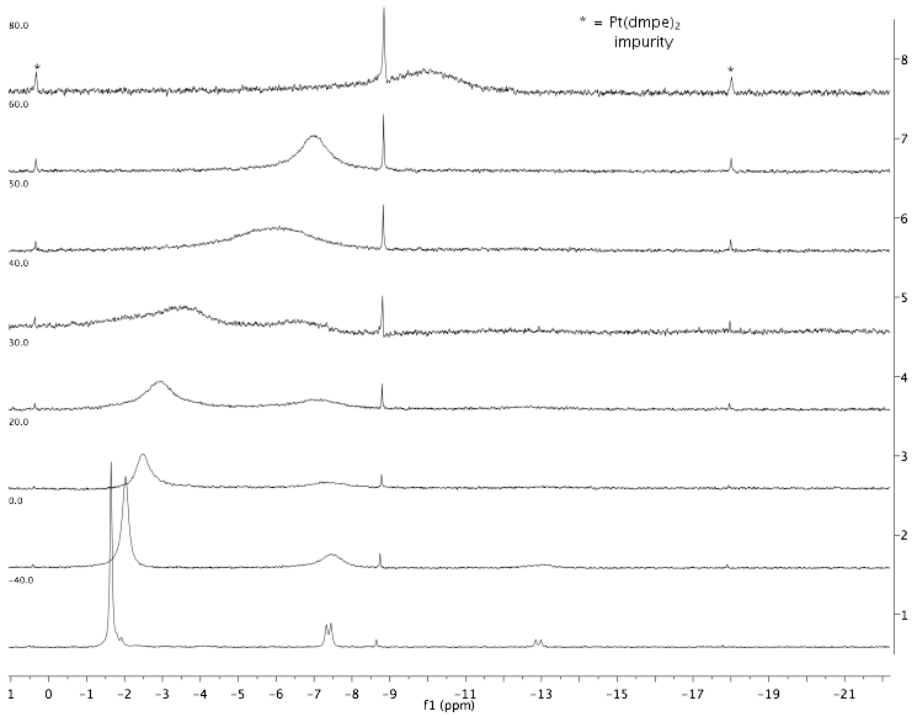


Figure S100. $^{31}P\{^{1}H\}$ NMR from -40 to 80 °C.

Reaction of [HPt][BAr^F_4] with BEt_3.

A J-Young NMR tube was charged with 21.5 mg (0.0158 mmol) [**HPt**][BAr^F_4] and ~0.6 mL C_6D_5Cl. 15.8 μL (0.0158 mmol) BEt_3 (1.0 M in hexanes) was added by syringe, and the tube was sealed. No precipitation was observed upon addition of the borane. NMR spectroscopy revealed no detectable change in line shape or chemical shift of the hydride.

Reaction of [Li][$Et_3BHBHEt_3$] + $[Pt]^{2+}$.

A small vial was charged with ~0.6 mL THF-d_8, 25.5 μL (0.0255 mmol) BEt_3 (1.0 M in hexanes), and 25.5 μL (0.0255 mmol) $LiHBEt_3$ (1.0 M in THF-d_8). The mixture was added to solid [**Pt**][PF_6]$_2$, and the reaction mixture transferred to a J-Young tube. NMR spectroscopy showed that $Pt^0(dmpe)_2$ was the major product (consistent with observed bubbling, presumably

of H_2), with the other P-containing product being a singlet at δ -0.7 with no Pt satellites. The ^{1}H NMR was mostly obscured by hexanes and THF, but the diagnostic broad doublet (-3.58, d, J_{PH} = 170 Hz) was observed in the reaction of [**HPt**]$^+$ with boranes was observed, consistent with the bridging borohydride perhaps playing a role in the reaction.

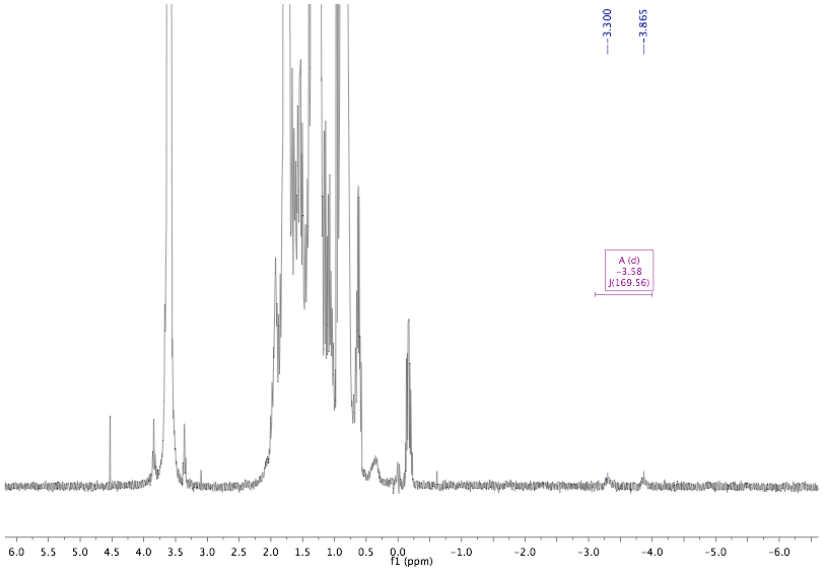


Figure S101. ^{1}H NMR.

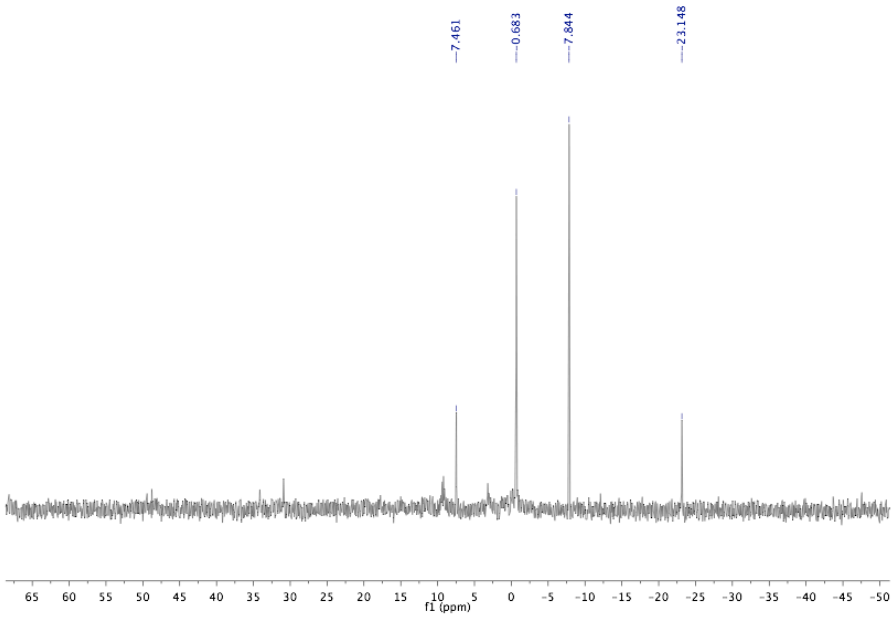


Figure S102. ^{31}P{^{1}H} NMR.

E. Reduction of *trans*-[$(Ph_2P(CH_2)_2B(C_8H_{14}))_2Mn(CO)_4$][$BF_4$] ([1-$E_2$-Mn][$BF_4$]).

Reaction of [1-E_2-Mn][BF_4] with 1 equiv $NaHBEt_3$.

To a rapidly stirring solution of 32 mg (0.034 mmol) [**1-E_2-Mn**][BF_4] in ~0.6 mL C_6D_5Cl was added 34 μL (0.034 mmol) $NaHBEt_3$ (1.0 M in toluene). The solution darkened slightly, and the mixture was transferred to an NMR tube. Spectroscopic analysis revealed conversion to a putative boroxycarbene species (^{1}H NMR δ 13.81, $^{31}P\{^1H\}$ NMR δ 61.0.). This species was not further characterized. When the reaction was run in THF-d_8, only a mixture of starting material and doubly reduced species (see below) was observed, indicating fast disproportionation is operative.

Reaction of [1-E_2-Mn][BF_4] with 1 equiv $[HPt(dmpe)_2]^+$.

To a stirring solution of 17.6 mg (0.0191 mmol) [**1-E_2-Mn**][BF_4] was added 12.2 mg [**HPt**][PF_6] partwise as a solid. The mixture was stirred for two minutes before being transferred to a J-Young NMR tube, at which time NMR spectroscopic analysis showed a mixture of the same boroxycarbene as in the preceding reaction, and cation starting material.

Reaction of [1-E_2-Mn][BF_4] with 2 equiv $NaHBEt_3$.

To a rapidly stirring solution of 37 mg (0.040 mmol) [**1-E_2-Mn**][BF_4] in ~0.6 mL THF-d_8 was added 80 μL (0.080 mmol, 2 equiv) $NaHBEt_3$ (1.0 M in toluene). The color of the reaction mixture changed from pale yellow to orange over the course of the addition, and became cloudy. The mixture was filtered through a sintered glass filter into an NMR tube, and the resulting spectra revealed one major asymmetric species. Some impurity, with small, broad resonances,

was apparent. Attempts to isolate and purify the material were met with failure, as removal of solvents and redissolution in THF showed marked decomposition. The nature of this decomposition remains unknown. The general structure of the product, containing a C-C bond and *cis*-oriented phosphines, was deduced by multinuclear and multidimensional NMR techniques. **^{1}H NMR** (THF-d_8, 600 MHz): δ 0.25 (1H), 0.55 (dd, J = 13.8, 27.7 Hz), 1.1-2.0 (m, overlapping with THF-d_8), 2.64 (dd, J = 13.0, 24.7 Hz, 1H), 2.8 (m, 1H), 2.93 (t, J = 13.3 Hz, 1H), 4.32 (d, J_{HH} = 16.6 Hz, 1H), 4.82 (d, J_{HH} = 16.6 Hz, 1H), 7.34 (m, 2H), 7.40 (t, J = 7.1 Hz, 2H), 7.64 (t, J = 8.1 Hz, 2H), 7.68 (m, 2H), 8.11 (t, J = 8.4 Hz, 2H). **^{31}P{^{1}H} NMR** (THF-d_8, 121 MHz): δ 52.8 (d, J_{PP} = 27.0 Hz), 60.1 (d, J_{PP} = 26.8 Hz). **^{13}C{^{1}H} NMR** (THF-d_8, 151 MHz): δ 13.05 (br), 15.38 (br), 23.35, 26.74, 27.25 (br), 27.55, 31.48 (d, JPC = 26.5 Hz), 31.87, 32.95, 33.61 (br), 33.92, 34.13 (d, J_{PC} = 14.2 Hz), 34.45 (br), 34.85, 34.98, 35.20, 92.85 (Mn=C(O-)*C*H$_2$O-), 127.77 (d, J_{PC} = 8.0 Hz), 127.94 (d, J_{PC} = 8.3 Hz), 128.13, 128.47 (d, J_{PC} = 8.0 Hz), 128.64, 129.63, 132.45 (d, J_{PC} = 7.4 Hz), 133.93 (d, J_{PC} = 8.2 Hz), 134.20 (d, J_{PC} = 8.7 Hz), 134.92 (d, J_{PC} = 10.5 Hz), 139.15 (d, J_{PC} = 25.9 Hz), 142.99 (d, J_{PC} = 37.0), 143.44 (d, J_{PC} = 20.0 Hz), 143.9 (d, J_{PC} = 38.3 Hz), 229.49 (dd, J_{PC} = 15.0, 17.8 Hz, CO), 231.11 (dd, J_{PC} = 23.6, 30.6 Hz, CO), 331.45 (m, Mn=*C*(O-)CH$_2$O-). **IR** (THF). 1935 (m), 1852 (s) cm^{-1}. A broad stretch at 1902 cm^{-1} appeared to be an impurity.

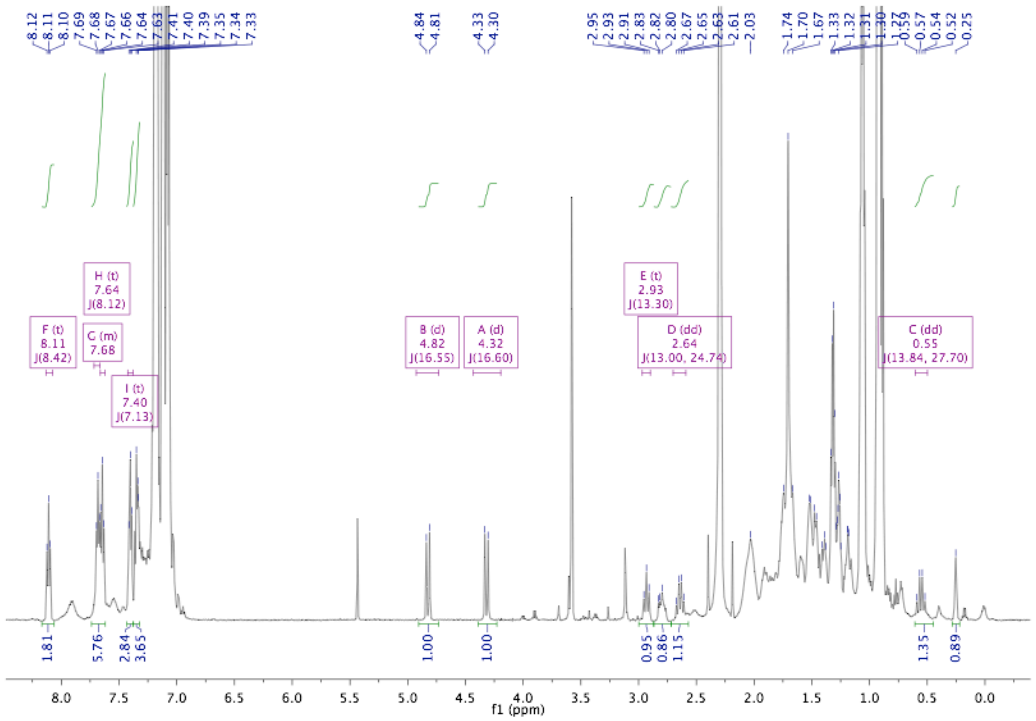


Figure S103. ^{1}H NMR.

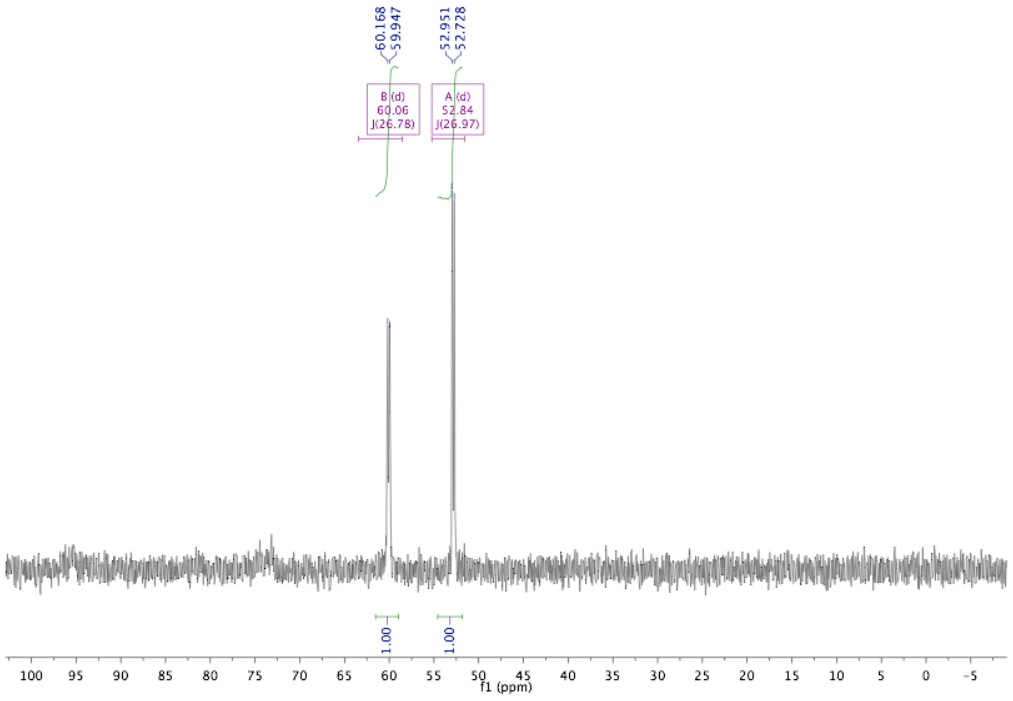


Figure S104. $^{31}P\{^{1}H\}$ NMR.

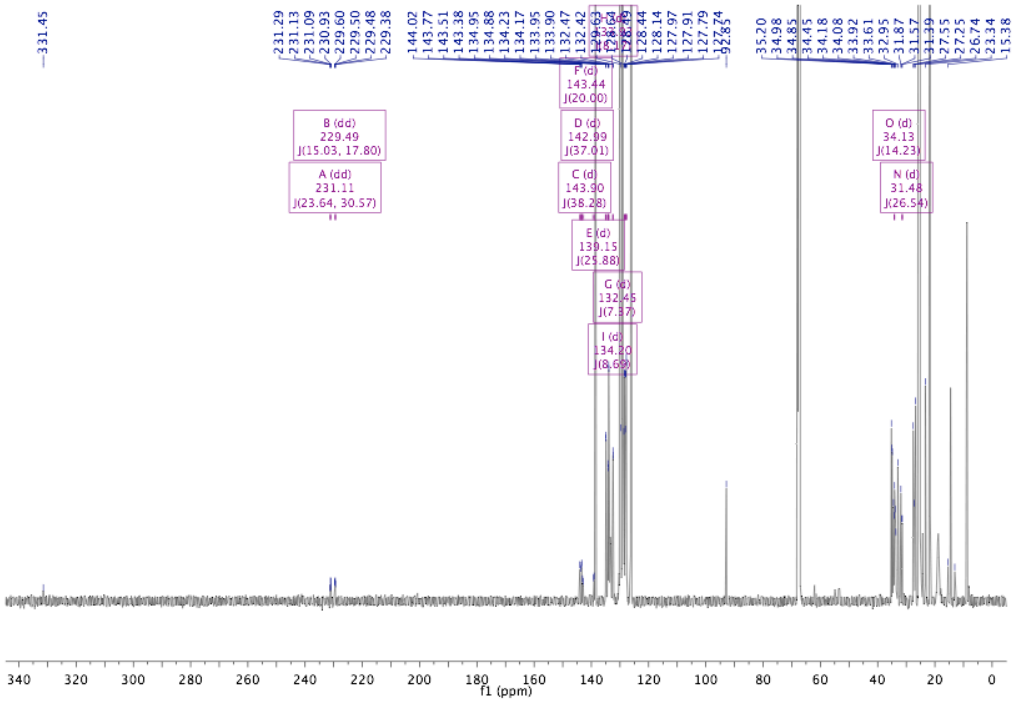


Figure S105. $^{13}C\{^{1}H\}$ NMR.

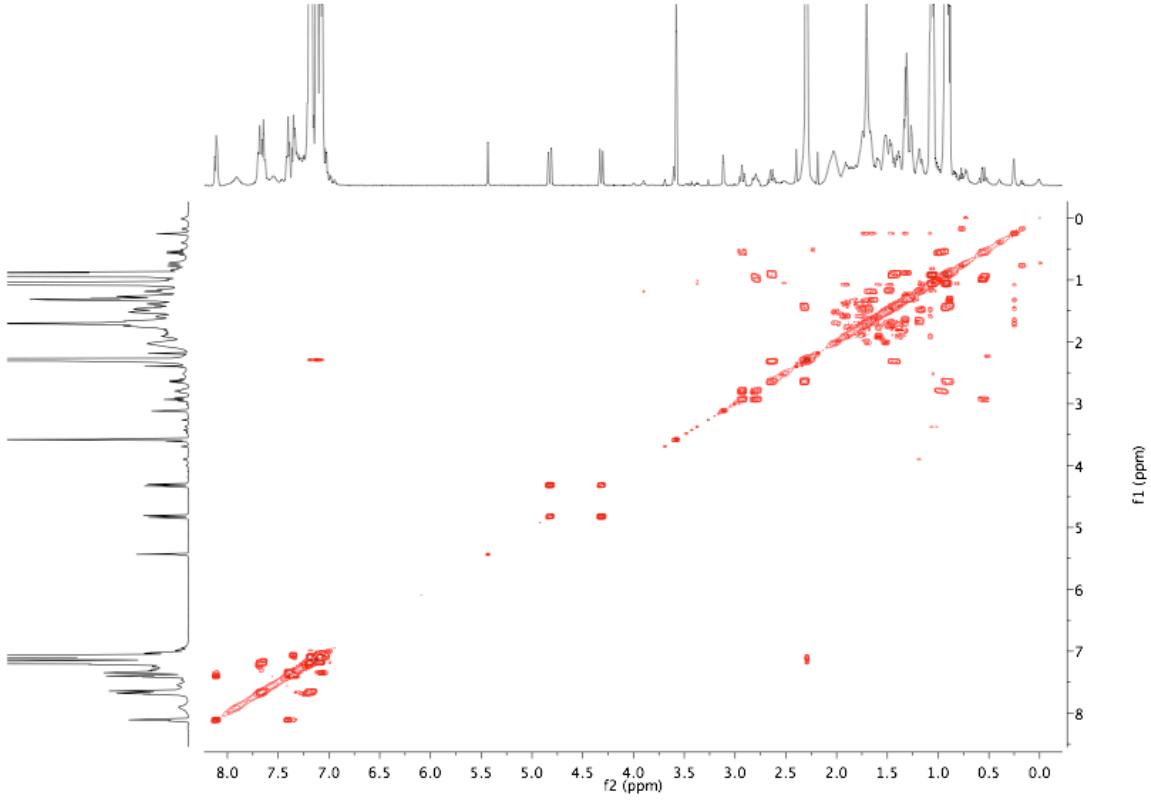


Figure S106. ^{1}H-^{1}H gCOSY.

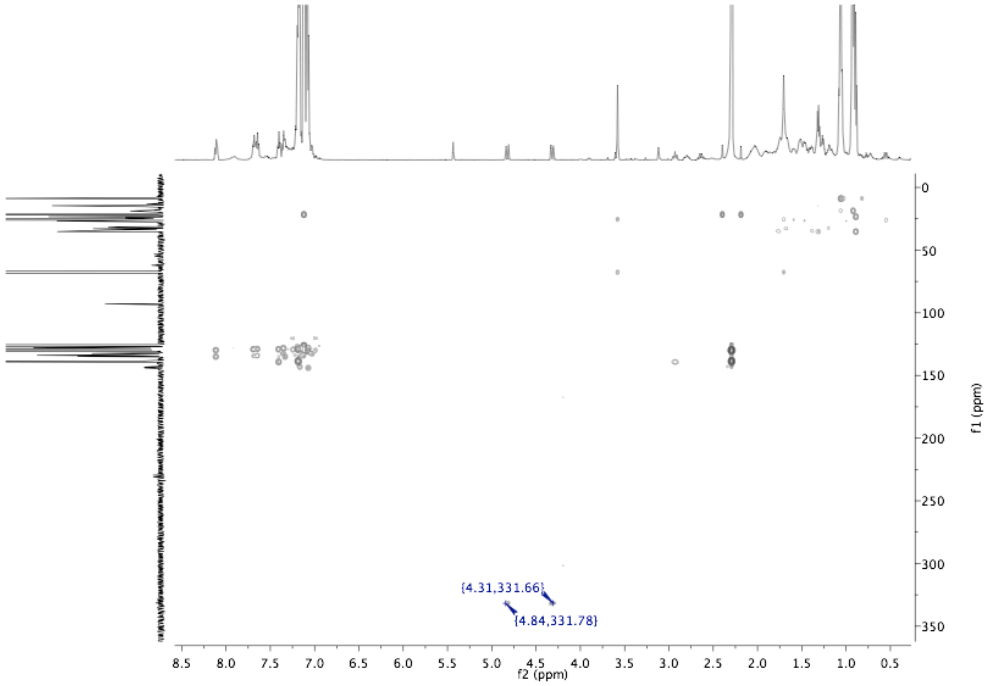


Figure S107. ^{1}H-^{13}C gHMBC.

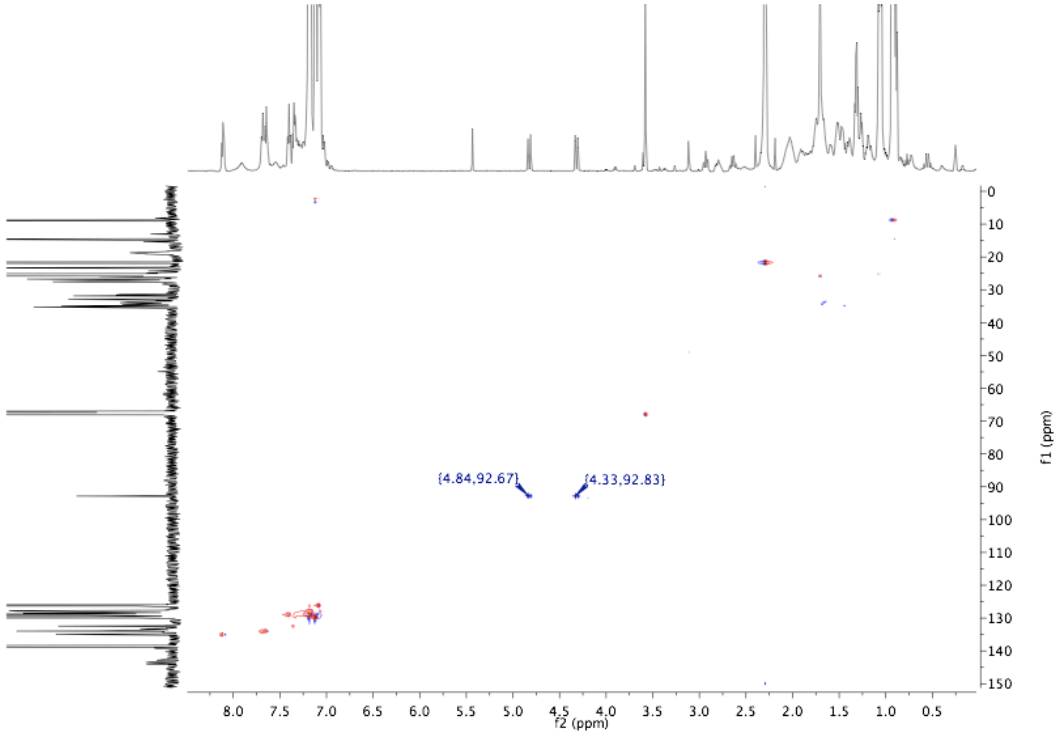


Figure S108. ^{1}H-^{13}C gHSQC.

Reaction of [1-E_2-Mn][BF_4] with 2 equiv [HPt][PF_6].

To a stirring ~0.6 mL THF-d_8 solution of 27.7 mg (0.030 mmol) was added 38.5 mg (0.060 mmol, 2 equiv) [**HPt**][PF_6] slowly as a solid. The solution darkened from yellow to orange with precipitation. After 30 minutes a mixture of C-C bond formed product [**3-E_2-Mn**]$^-$, starting cation, and unreacted [**HPt**]$^+$ were observed, closely resembling the spectra obtained using $NaHBEt_3$. Some minor variability in the chemical shifts is expected when changing the cation from Na^+ to [**Pt**]$^{2+}$ or [**HPt**]$^+$. Interestingly, the reaction did not proceed to completion overnight, possibly because monocationic [**HPt**]$^+$ was favored as the countercation over insoluble [**Pt**]$^{2+}$.

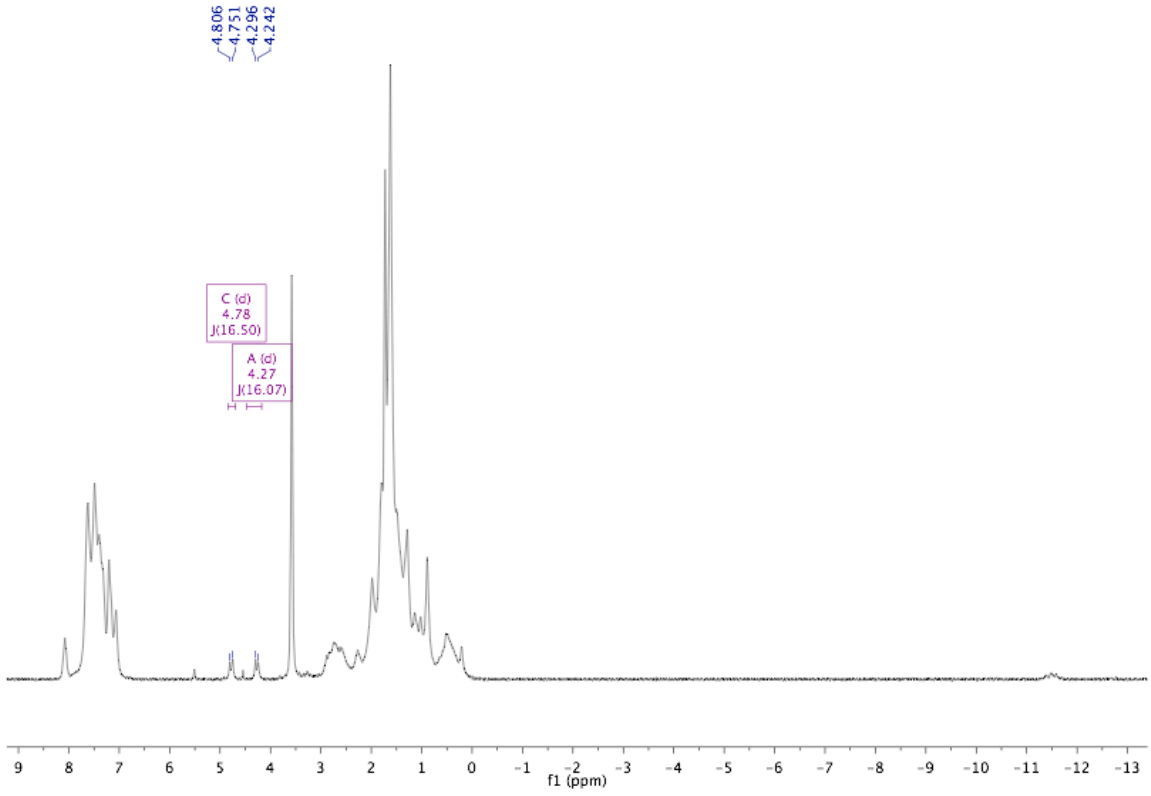


Figure S109. ^{1}H NMR.

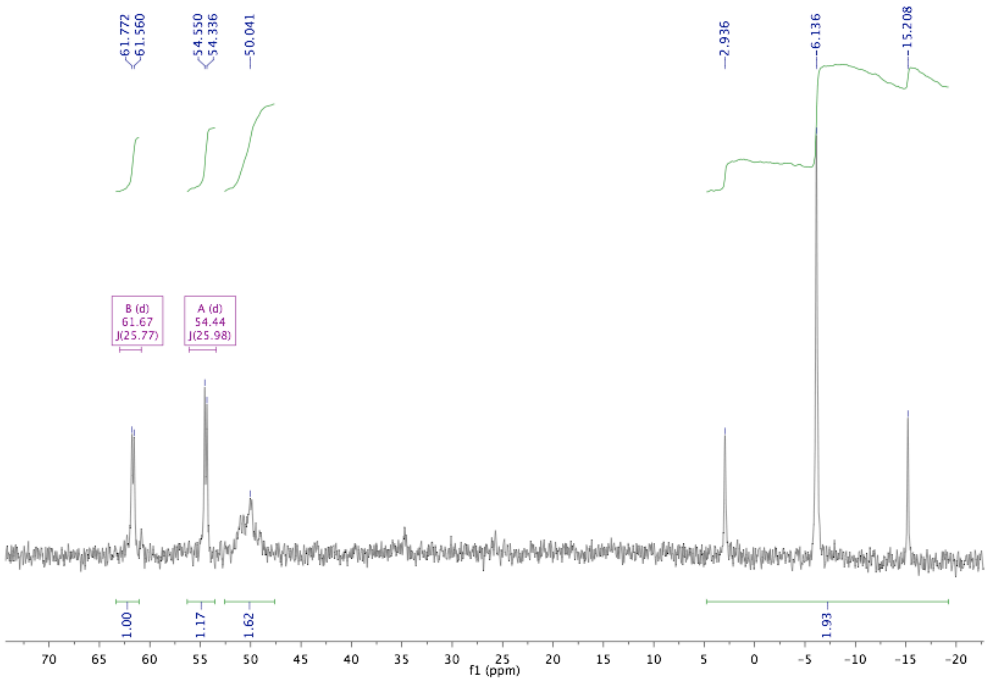


Figure S110. $^{31}P\{^{1}H\}$ NMR.

F. Reduction of *trans*-[($Ph_2P(CH_2)_3B(C_8H_{14})$)$_2$Re(CO)$_4$][$BF_4$] ([1-$P_2$][$BF_4$]).

Reaction of [1-P_2][BF_4] with 1 equiv $NaHBEt_3$.

A scintillation vial was charged with 40.7 mg (0.0376 mmol) cation [**1-P_2**][BF_4] and 0.5 mL C_6D_5Cl. With rapid stirring, 37.6 μL (0.0376 mmol) $NaHBEt_3$ (1.0 M in toluene) was added dropwise. The colorless solution turned yellow. The reduced species, [**2-P_2**]$_n$, synthesized *in situ* in this manner was stable for ~ 24 hours, after which time a significant amount of white precipitates had formed. [**2-P_2**]$_n$ could be characterized by NMR spectroscopy in the presence of toluene and BEt_3 from the borohydride reagent. **^{1}H NMR** (C_6D_5Cl, 300 MHz): δ 1.36 (br, 12H), 1.7-2.1 (br m, 24H), 2.65 (br, 4H, $Ph_2PCH_2CH_2CH_2B(C_8H_{14})$), (7.0-7.2 m, toluene obscures $Ph_2PCH_2CH_2CH_2B(C_8H_{14})$ peak), 7.5 (m, 8H, $Ph_2PCH_2CH_2CH_2B(C_8H_{14})$), 14.09 (s, 1H, Re-C*H*O). **$^{31}P\{^{1}H\}$ NMR** (C_6D_5Cl, 121 MHz): δ 6.7 (br). **$^{13}C\{^{1}H\}$ NMR** (C_6D_5Cl, 125 MHz): 19.4

(br), 20.3, 24.7, 26.4, 28.7 (br), 32.9, 128.6 (t, J_{PC} = 4.6 Hz), 130.3, 132.0 (t, J_{PC} = 4.4 Hz), 136.4 (br m, *i-Ph*), 194.0 (m, Re-*C*O), 196.4 (m, Re-*C*O), 282.7 (v. br, Re-*C*HO).

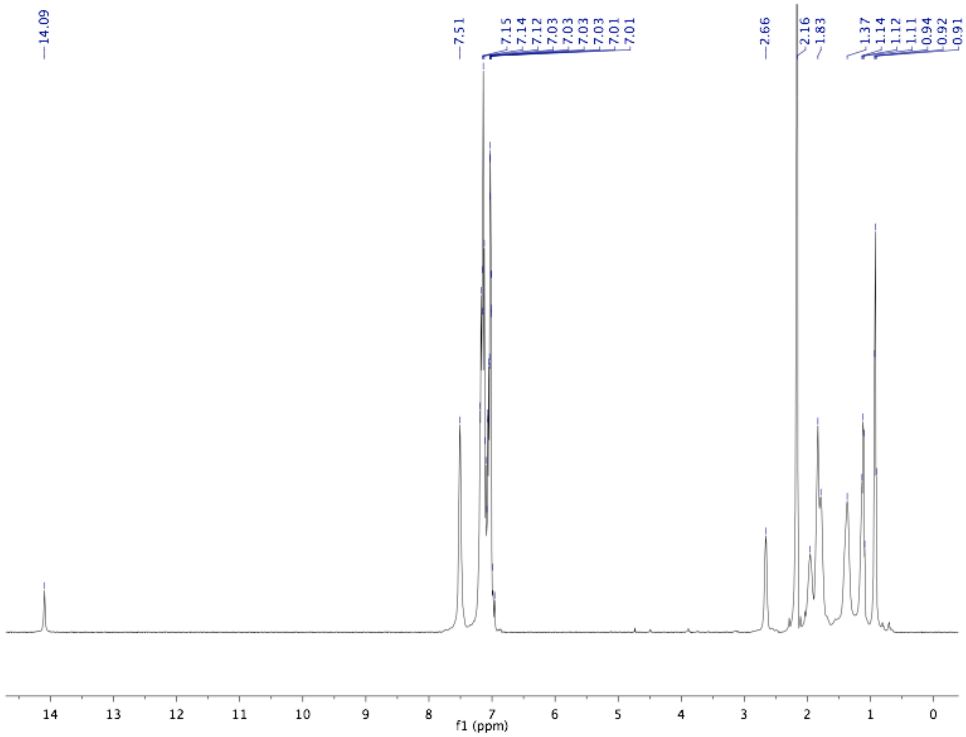


Figure S111. ^{1}H NMR.

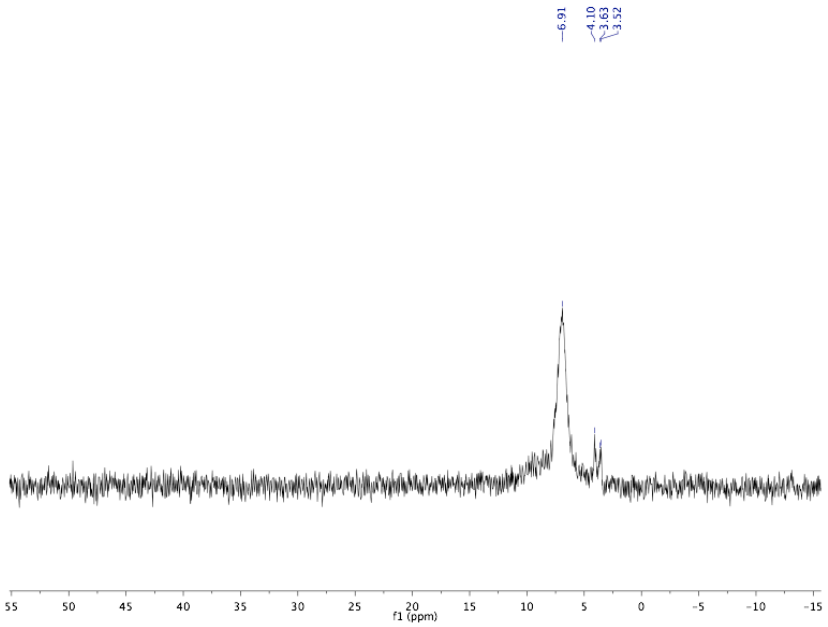


Figure S112. ^{31}P{^{1}H} NMR.

The solids that precipitate over time are assigned as oligomeric isomers of [**2-P$_2$**]$_n$. While these solids are insoluble in most common organic solvents, they do dissolve upon addition of pyridine, giving a formyl complex wherein the pendant boranes are bound by pyridine, **2-P$_2$•2pyr**. This species was characterized by NMR, but decomposition (~80% Re-H after 18 hours) precluded isolation. **^{1}H NMR** (C_6D_5Cl, 300 MHz): δ 1.00 (br, 6H), 1.36 (br, 8H), 1.6-2.1 (br m, 22H), 2.47 (m, 4H), 7.47 (m, 8H), 8.12 (4H, BR_3-*py*), 15.00 (1H, Re-C*H*O). Some aryl peaks are obscured by toluene. **^{31}P{^{1}H} NMR** (C_6D_5Cl, 121 MHz): δ 6.2.

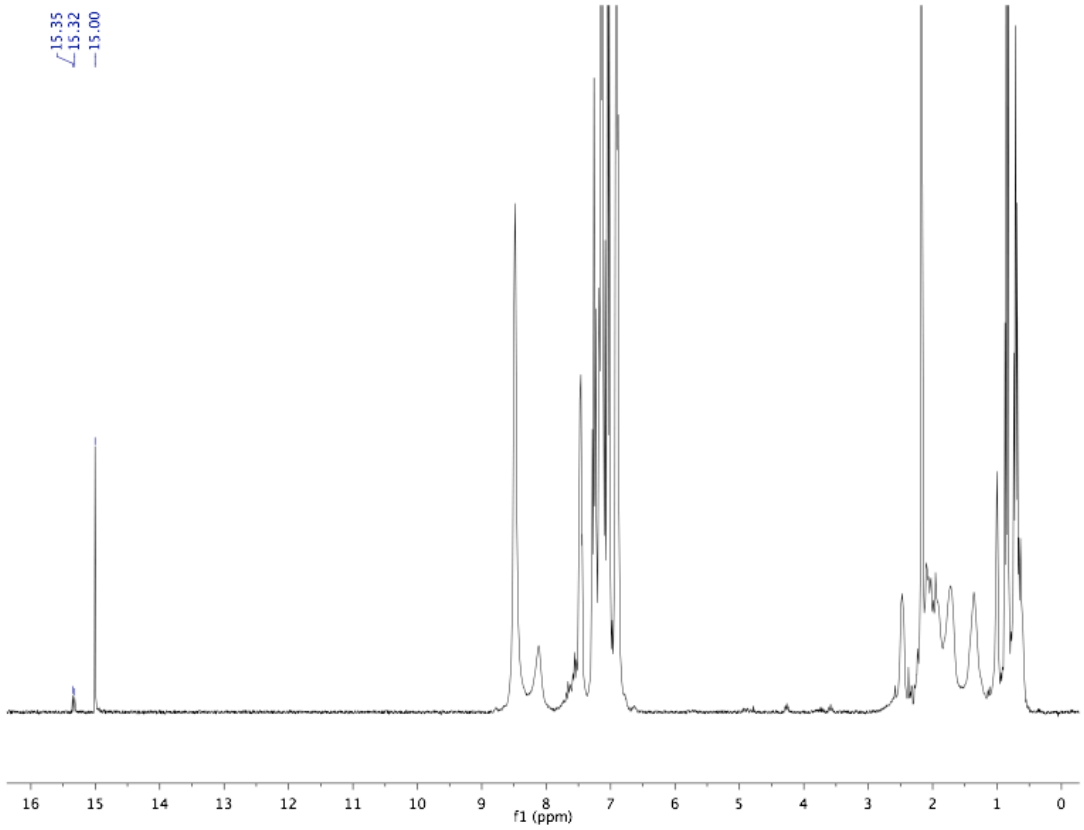


Figure S113. ^{1}H NMR.

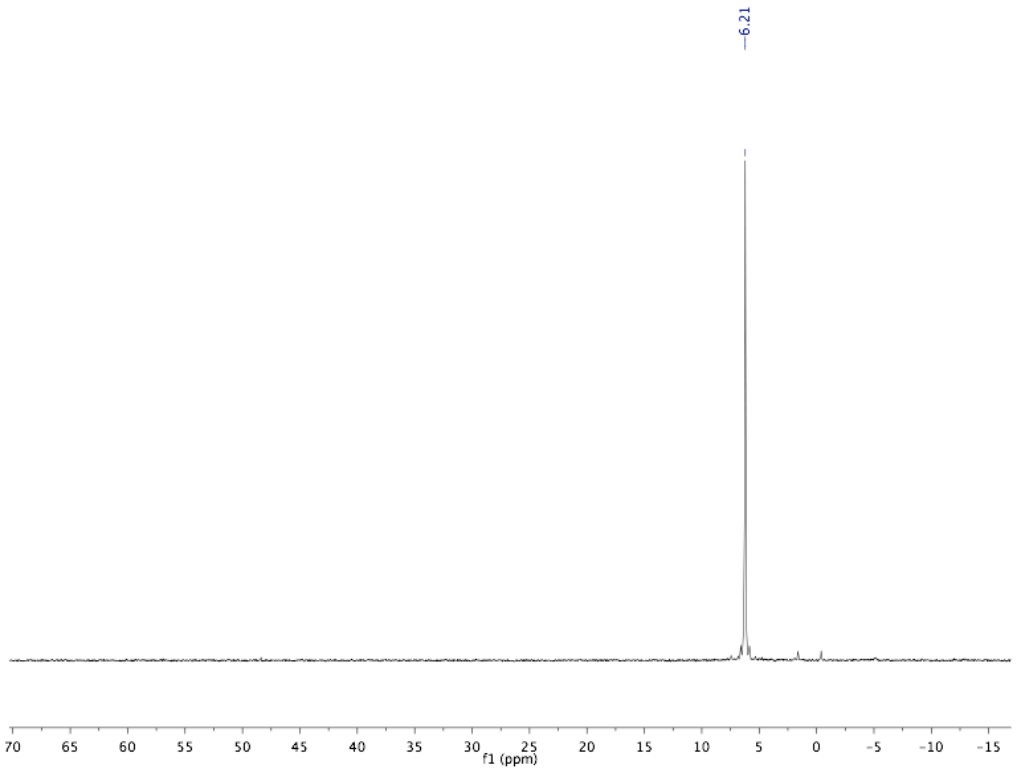


Figure S114. $^{31}P\{^{1}H\}$ NMR.

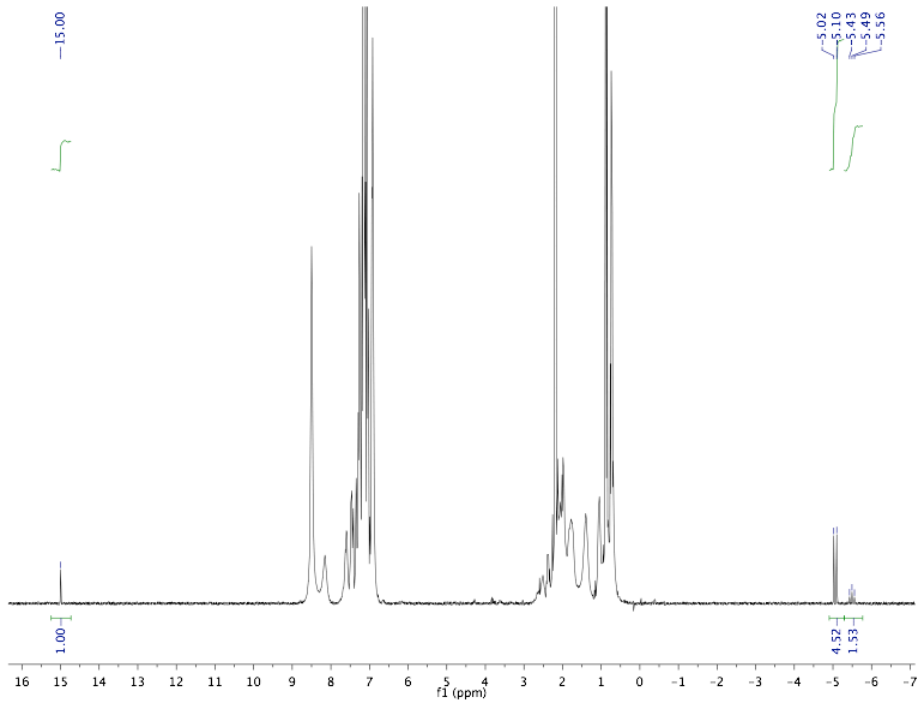


Figure S115. ^{1}H NMR after 18 hours.

Reaction of [1-P_2][BF_4] with 2 equiv. $NaHBEt_3$.

A variety of hydride sources and conditions were screened, and after workup there were always at least two products. A representative preparation involved dissolving 120 mg (0.110 mmol) cation [**1-P_2**][BF_4] in 2 mL C_6H_5Cl with stirring, followed by dropwise addition of 110 μL (0.110 mmol, 1 equiv) $NaHBEt_3$ (1.0 M in toluene). The mixture was stirred briefly, then allowed to stand for 10 minutes. After filtration, to the yellow solution was added 38 mg (0.105 mmol, 0.95 equiv) dibenzo-18-crown-6, followed by another (0.110 mmol, 1 equiv) $NaHBEt_3$ (1.0 M in toluene), dropwise by syringe. The clear yellow solution was stirred for two hours, filtered again, and the solvents removed *in vacuo*. After washing with Et_2O, the solids were extracted in THF and the solvents removed *in vacuo*. The crude THF fraction included a number of products, including two doublets in the ^{1}H NMR at δ 4.63 (J_{HH} = 17.3 Hz) and 4.78 (J_{HH} = 16.8 Hz), similar to those observed in other C-C bond-formed products. Isolation of the desired product was unsuccessful, however.

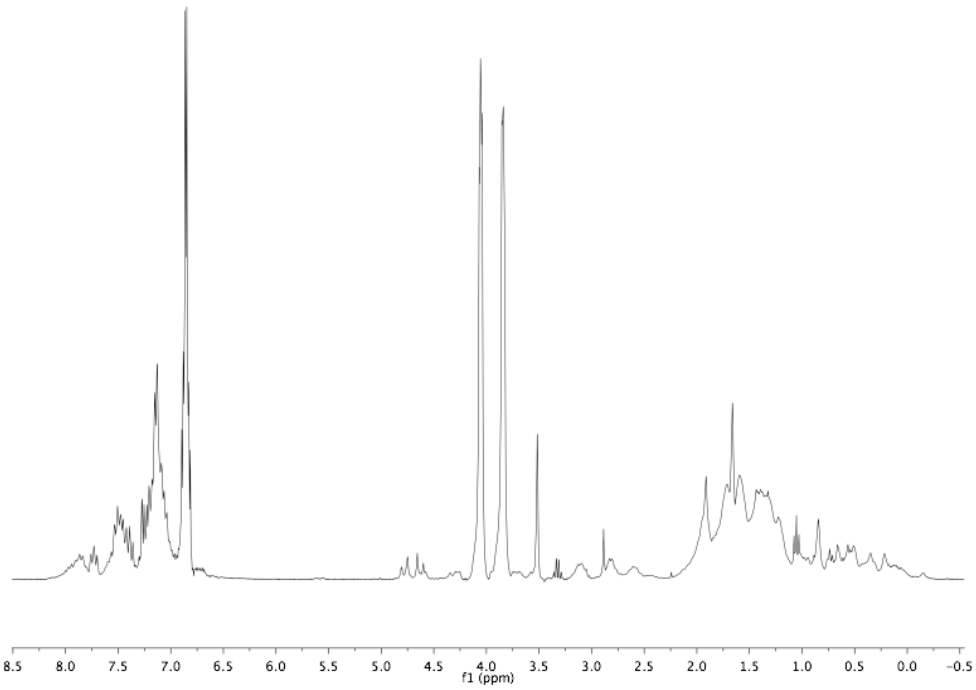


Figure S116. ^{1}H NMR.

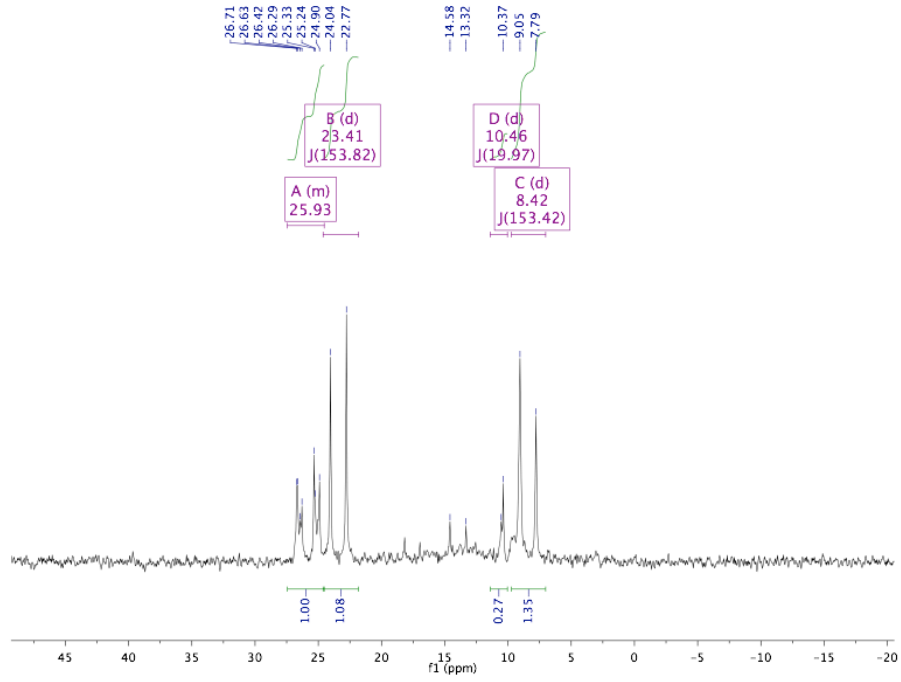


Figure S117. $^{31}P\{^{1}H\}$ NMR.

NMR-scale Reaction of [1-P_2][BF_4] with 1 equiv [HPt][PF_6].

Under a nitrogen atmosphere, 28.5 mg (0.026 mmol) cation [**1-P_2**][BF_4] was dissolved in 0.5 mL C_6D_5Cl in a 10 mL scintillation vial with stirring. Solid [**HPt**]$^+$ (16.9 mg, 0.026 mmol) was added as a solid portionwise. After stirring for ten minutes, the cloudy solution was filtered through microporous glass into an NMR tube, and spectra acquired, showing relatively high conversion to carbene **2-P_2** (spectroscopic details above) in ~90% yield by ^{31}P integration.

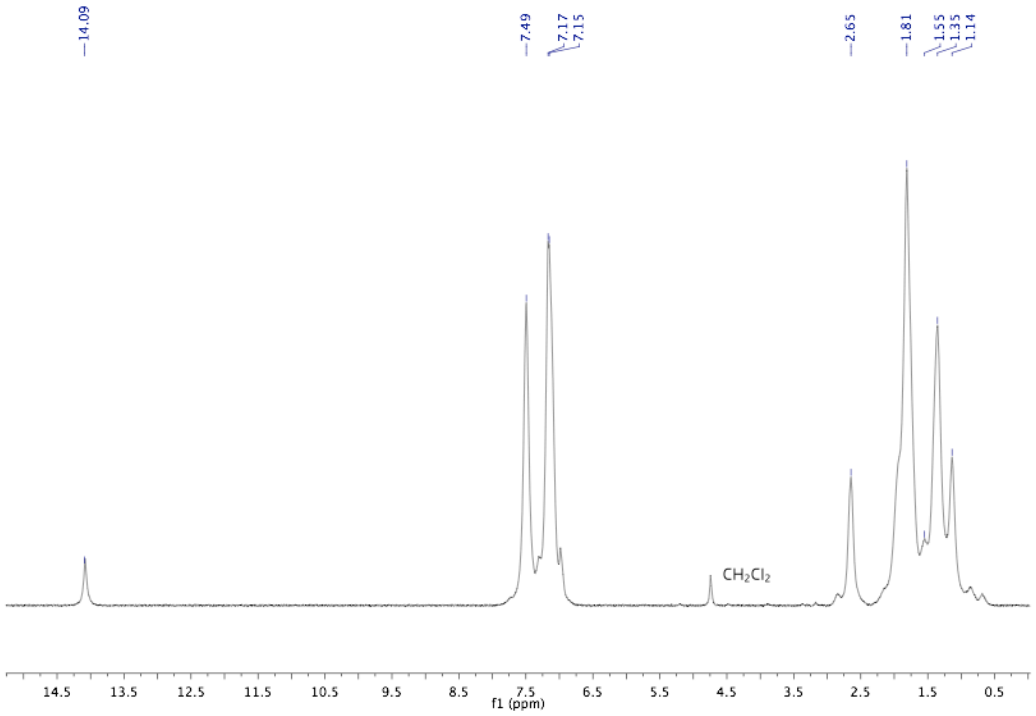


Figure S118. ^{1}H NMR.

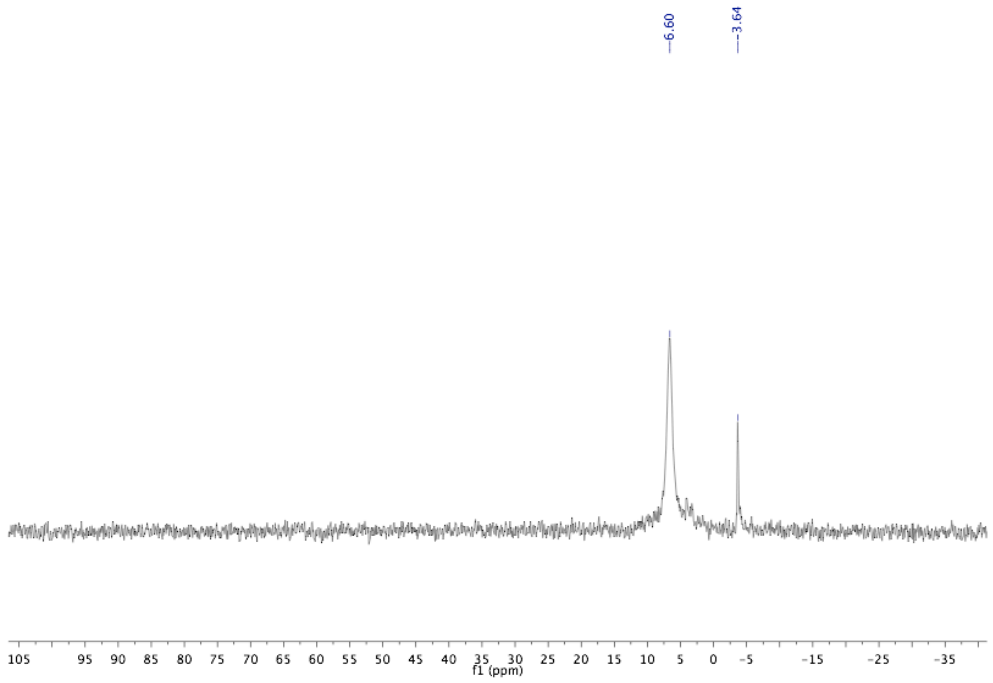


Figure S119. $^{31}P\{^{1}H\}$ NMR.

Reaction of [1-P_2][BF_4] with 2 equiv [HPt][PF_6].

19.3 mg (0.017 mmol) [**1-P_2**][BF_4], 22.9 mg (0.0357 mmol, 2 equiv) [**HPt**]$^+$, 4.5 mg (0.017 mmol) 18-crown-6, and 2.9 mg (0.017 mg) $NaPF_6$ were added to a small vial, and dissolved in C_6D_5Cl. The mixture was transferred to a J-Young NMR tube, and the reaction was monitored by ^{1}H and ^{31}P NMR. After initial formation of carbene **2-P_2**, no further reduction was observed over 3 days. The crown ether and $NaPF_6$ were added in an attempt to favor formation of soluble coupled products. In a separate experiment, only cation [**1-P_2**][BF_4] and 2 equiv [**HPt**]$^+$ were mixed, and the same results were observed.

V. Equilibrium Studies of Bis(phosphine) Complexes.

Reaction of 2-E_2 with [Pt][PF_6]$_2$.

To a stirring solution of 22.2 mg (0.021 mmol) [**1-E_2**][BF_4] in ~0.6 mL C_6D_5Cl was added 21 μL (0.021 mmol) $NaHBEt_3$ (1.0 M in toluene) dropwise by syringe. After stirring for a roughly one minute, the pale yellow solution was transferred to a J-Young NMR tube that had been charged with 16.5 mg (0.021 mmol) [Pt(dmpe)$_2$][PF_6]$_2$. The white Pt salt did not appear to dissolve. Monitoring by NMR showed no reaction over 24 hours.

Reaction of 2-M_2 with [1-E_2]$^+$.

Boroxycarbene **2-M_2** was prepared by addition of solid [**HPt**][PF_6] (12.4 mg, 0.0194 mmol) to a stirring 0.6 mL C_6D_5Cl solution of 31.3 mg (0.0194 mmol) [**1-M_2**][$B(C_6F_5)_4$] and 8 mg (0.075 mmol, 3.75 equiv) $NaBF_4$. The mixture was transferred the a J-Young NMR tube, and monitored by multinuclear NMR spectroscopy. After 22 hours, all [**1-M_2**]$^+$ had been converted to **2-M_2** in good yield. Once the reaction had run to completion, the contents of the NMR tube were, under a N_2 atmosphere, filtered through sintered glass onto 20.4 mg (0.0194 mmol) solid [**1-E_2**][BF_4]. NMR spectroscopy showed only unreacted **2-M_2** and [**1-E_2**]$^+$ over 4 hours.

Reaction of 2-E_2 with [1-M_2]$^+$.

Boroxycarbene **2-E_2** was prepared by dropwise addition of 21.8 μL (0.0218 mmol) $NaHBEt_3$ (1.0 M in toluene) to a stirring ~0.6 mL C_6D_5Cl solution of 23.0 mg (0.0218 mmol) [**1-E_2**][BF_4]. ^1H and ^{31}P NMR spectroscopy showed clean conversion to **2-E_2**. The tube was returned to the glovebox, where it was poured onto 36.6 mg (0.0227 mmol, 1.04 equiv) [**1-M_2**]$^+$. Multinuclear NMR spectroscopy revealed complete hydride transfer had occurred, with no **2-E_2** remaining,

and instead a mixture of **2-M$_2$**, unreacted [**1-M$_2$**]$^+$, and [**1-E$_2$**]$^+$. The observed hydride transfer is consistent with the preceding experiment in which the reverse reaction did not proceed to any appreciable extent.

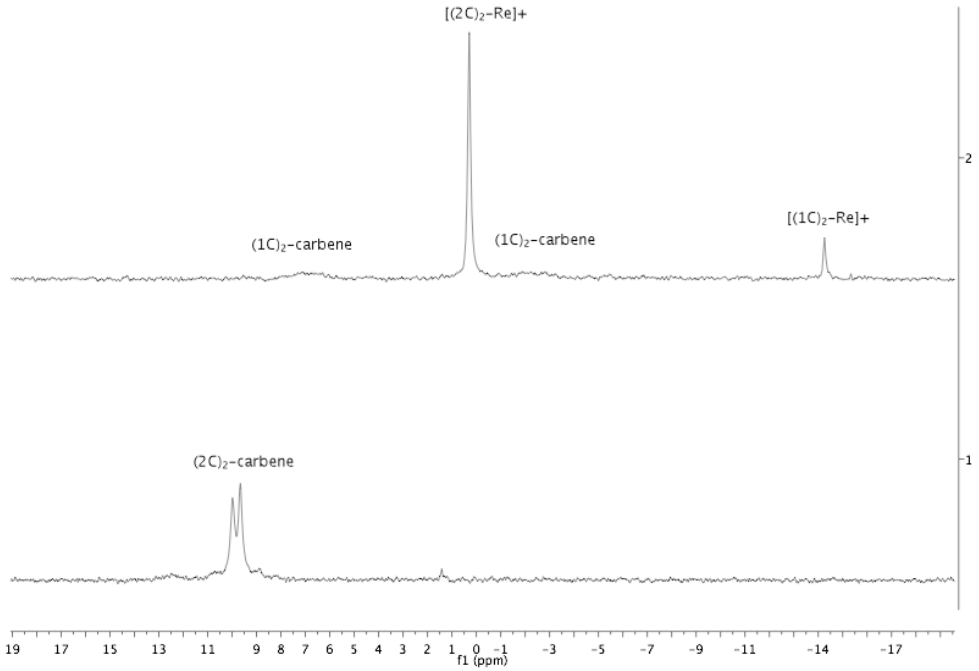


Figure S120. $^{31}P\{^1H\}$ NMR, showing formation of **2-E$_2$** (bottom) and after treatment with [**1-M$_2$**]$^-$ (top).

Reaction of 2-E$_2$ with [1-P$_2$]$^+$.

Boroxycarbene **2-E$_2$** was prepared by dropwise addition of 25.6 μL (0.0256 mmol) $NaHBEt_3$ (1.0 M in toluene) to a stirring ~0.6 mL C_6D_5Cl solution of 27.0 mg (0.0256 mmol) [**1-E$_2$**][BF_4]. After stirring for 5 minutes after hydride addition, the solution was added to solid [**1-P$_2$**][BF_4], and the mixture was transferred to a J-Young NMR tube. After 30 minutes, ^1H and $^{31}P\{^1H\}$ NMR spectroscopy revealed a mixture of all possible constituents, [**1-E$_2$**]$^+$, **2-E$_2$**, [**1-P$_2$**]$^+$, and **2-P$_2$**, in similar quantities. The ^{31}P NMR signals of **2-P$_2$** and [**1-E$_2$**]$^+$ were slightly broadened, and the Re-

C*H*O signal of **2-P$_2$** in the ^{1}H NMR was significantly broadened, possibly signifying an intermolecular interaction between these species. The precise speciation is unknown, as probably fluxional, involving different species coordinating to the Re-CHO oxygen. Due to the broadness and uncertainty in ^{31}P NMR delay times, rigorous integration was not pursued; $K_{eq} \sim 1$ was obtained by ^{31}P NMR integration. The equilibrium mixture was stable for at least 4.5 hours.

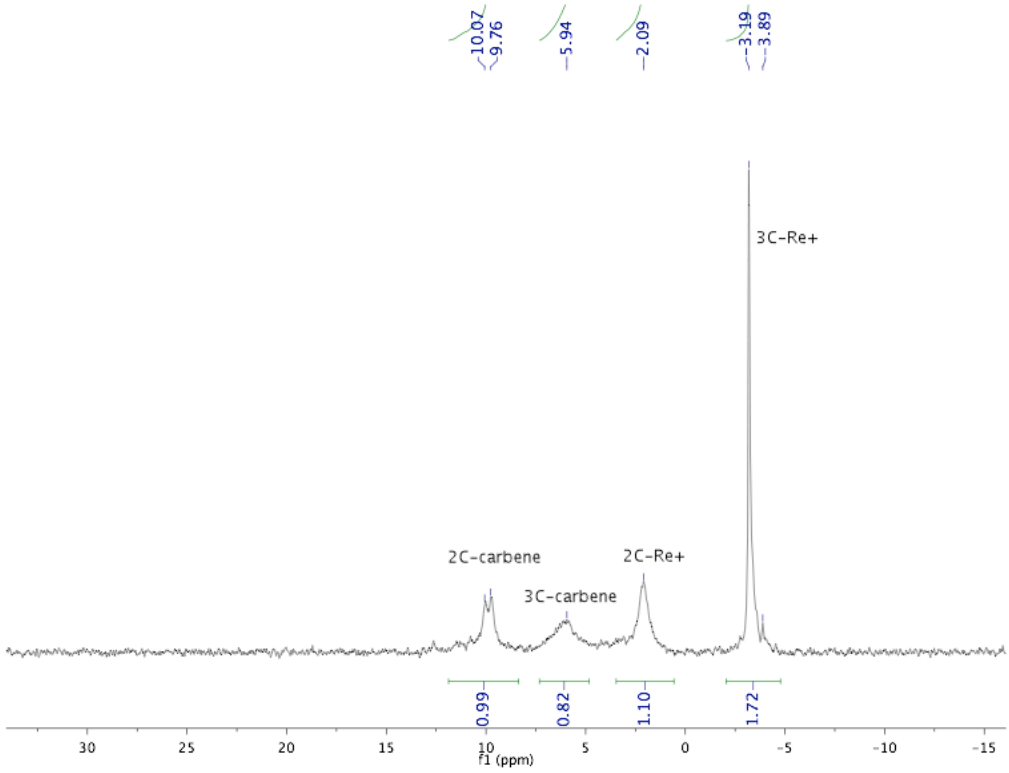


Figure S121. ^{31}P NMR after equilibrium.

Reaction of 2-P$_2$ with [1-E$_2$]$^+$.

Boroxycarbene **2-P$_2$** was prepared by dropwise addition of 26.4 µL (0.0264 mmol) $NaHBEt_3$ (1.0 M in toluene) to a stirring ~0.6 mL C_6D_5Cl solution of 28.5 mg (0.0264 mmol) [**1-P$_2$**][BF_4]. The solution was added to a J-Young NMR tube and multinuclear NMR spectroscopy showed clean conversion to **2-P$_2$**. The tube was returned to the glovebox, the contents poured onto 27.8 mg

(0.0264 mmol) solid [**1-E$_2$**][BF$_4$], and the reaction mixture returned to the NMR tube. After 30 minutes, an equilibrium mixture of all the constituents was achieved ([**1-E$_2$**]$^+$, **2-E$_2$**, [**1-P$_2$**]$^+$, and **2-P$_2$**). The spectra were essentially the same as in the preceding reaction, with K_{eq} again roughly 1 (^{31}P NMR integration). The equilibrium mixture was stable for at least 3.5 hours.

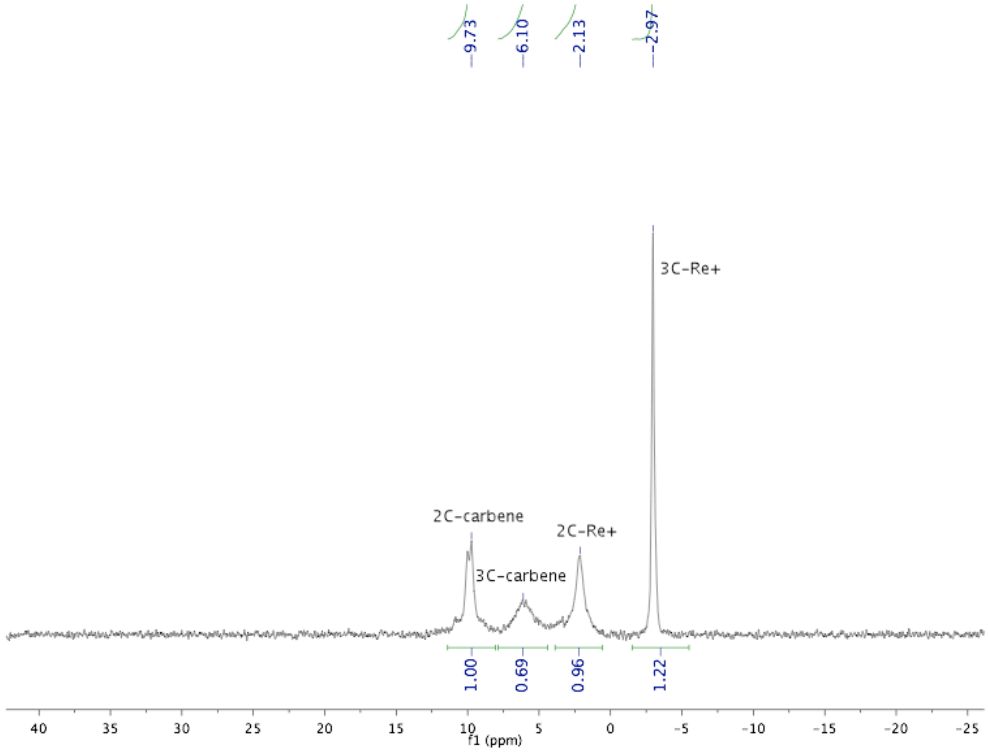


Figure S122. ^{31}P{^{1}H} NMR.

Reaction of 2-E$_2$ with [1-Ph$_2$][BAr$^F{}_4$].

A vial was charged with 25.2 mg (0.0239 mmol) [**1-E$_2$**][BF$_4$] and ~0.6 mL C_6D_5Cl. With stirring, 15.3 mg (0.0239 mmol) [**HPt**][PF$_6$] was added as a solid, partwise. The colorless solution turned yellow with precipitation and was stirred for ~10 min, after which time the reaction mixture was added to 40.3 mg (0.0239 mmol) solid [**1-Ph$_2$**][BAr$^F{}_4$]. NMR spectroscopy revealed a mixture of all the possible constituents, in roughly equal parts, with a estimated K_{eq} ~ 1. As in the case of **2-P$_2$**, **2-Ph$_2$** showed shifted resonances in the ^{1}H NMR (Re-CHO) and ^{31}P NMR, with the ^{31}P NMR

signal for [**1-E$_2$**]$^+$ being broadened, perhaps suggesting some interaction of **2-Ph$_2$** with one of the pendent boranes.

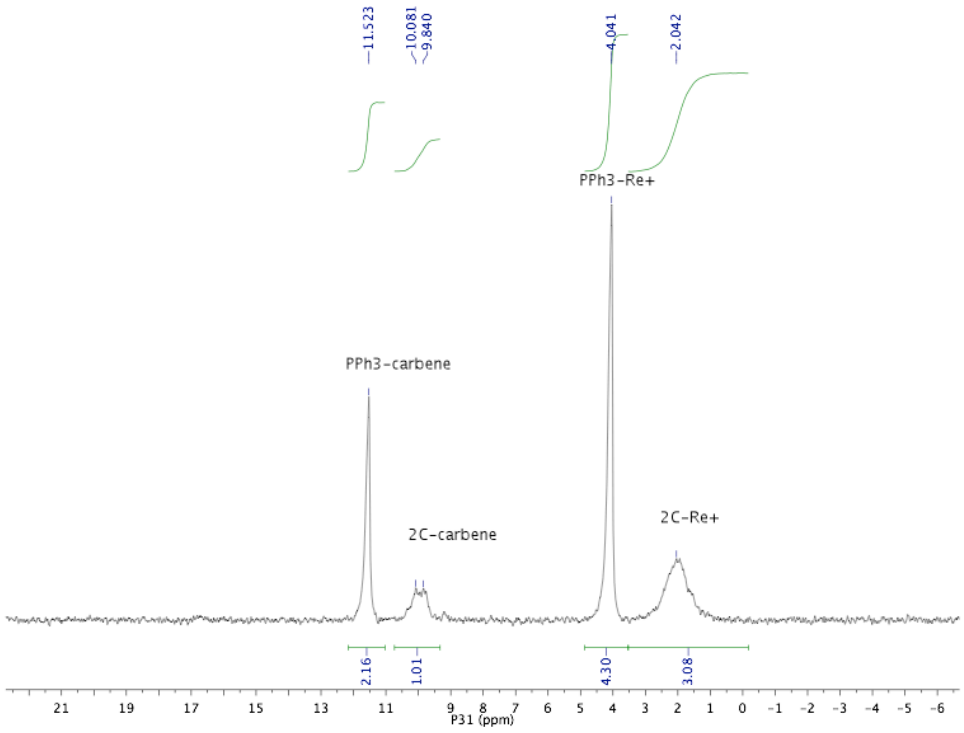


Figure S123. $^{31}P\{^1H\}$ NMR.

Reaction of 2-Ph$_2$ with [1-E$_2$][BF$_4$].

To a stirring solution of 41.4 mg (0.0246 mmol) [**1-Ph$_2$**][BAr$^F_4$] in C_6D_5Cl was added 24.6 μL (0.0246 mmol) $NaHBEt_3$ (1.0 M in toluene) dropwise. The mixture turned yellow and was stirred for 5 min, then added to 25.9 mg (0.0246 mmol) [**1-E$_2$**][BF_4]. The mixture was transferred to a J-Young tube and shaken well. NMR spectroscopy showed a mixture of both Re-CHO species and both cations, in roughly equal amounts, giving a rough $K_{eq} \sim 1$. As in the preceding reaction, the resonances of **2-Ph$_2$** did not match previous syntheses exactly, suggesting some interaction with the pendent boranes of [**1-E$_2$**]$^+$.

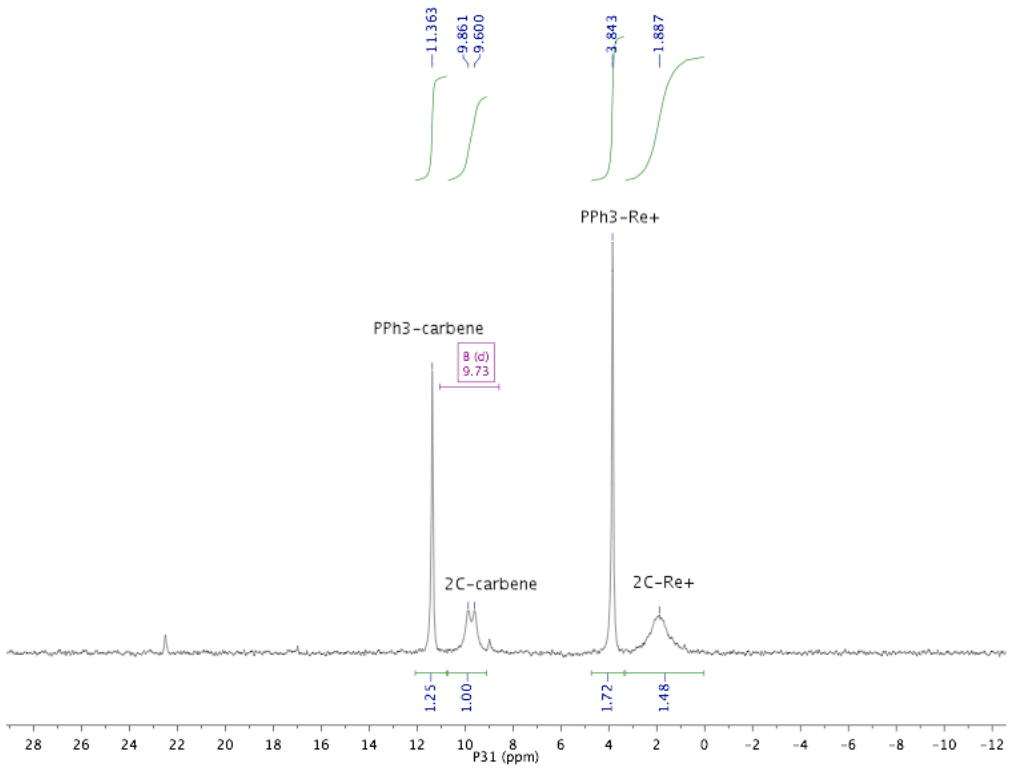


Figure S124. $^{31}P\{^{1}H\}$ NMR.

Reaction of 2-E_2 with 2-M_2.

Boroxycarbene **2-E_2** was first prepared, by addition of 21.0 mg (0.0327 mmol) solid [**HPt**]$^+$ to a stirring ~0.6 mL C_6D_5Cl solution of 52.8 mg (0.0327 mmol) [**1-M_2**][$B(C_6F_5)_4$] and 16.0 mg (0.0327 mmol) tetraheptylammonium tetrafluoroborate. The solution was transferred to a J-Young NMR tube, and was allowed to react overnight. A few days later, boroxycarbene **2-E_2** was prepared by dropwise addition of 32.7 μL (0.0327 mmol) $NaHBEt_3$ (1.0 M in toluene) to a stirring ~0.4 mL C_6D_5Cl solution of 34.5 mg (0.0327 mmol) [**1-E_2**][BF_4]. The preformed **2-M_2** was returned to the glove box (NMR spectroscopy showed no decomposition during the days after preparation), and the contents of the tube were poured onto the solution containing **2-E_2**. The reaction mixture was filtered through sintered glass into a J-Young NMR tube, and

multinuclear NMR spectra were obtained, showing high conversion to the further reduced confused alkyl [**5**]$^-$ and cation [**1-E$_2$**]$^+$ (resulting from hydride transfer from **2-E$_2$**). A small amount of carbene **2-E$_2$** remained, along with small amounts of residual [**HPt**]$^+$ from the synthesis of **2-M$_2$**.

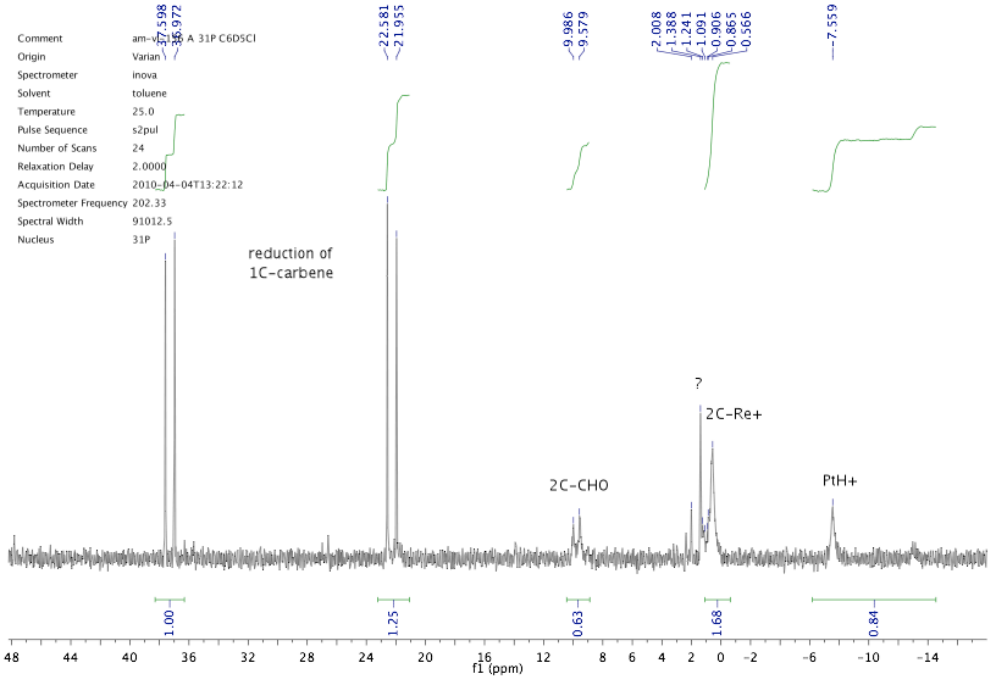


Figure S125. $^{31}P\{^1H\}$ NMR.

VI. Reductions of Monophosphine Complexes.

A. Reduction of [(PPh$_3$)Re(CO)$_5$][OTf] ([1-Ph$_1$][OTf]).

Reaction of [1-Ph$_1$][OTf] with 1 equiv [HPt][PF$_6$].

A small vial was charged with 16.7 mg (0.0225 mmol) [**1-Ph$_1$**][OTf] and ~0.6 mL C_6D_5Cl. With stirring, 14.4 mg (0.0225 mmol) [**HPt**][PF_6] was slowly added, and the reaction mixture transferred to a J-Young NMR tube. After 20 minutes, ^{1}H NMR spectroscopy revealed a mixture

of ~2:1 formyl:hydride, which converted almost entirely to hydride after 1.5 hours (~1:21 formyl:hydride). All formyl was consumed after 4 hours.

Reaction of [1-Ph$_1$][BAr$^F_4$] with 1 equiv [HPt][BAr$^F_4$].

A J-Young tube was charged with 31.3 mg (0.0215 mmol) [**1-Ph$_1$**][BAr$^F_4$], 29.2 mg (0.0215 mmol) [**HPt**][BAr$^F_4$], and ~0.6 mL C_6D_5Cl. Monitoring by NMR spectroscopy revealed no detectable reaction after 15 minutes, and only partial conversion to **2-Ph$_1$** after 3 hours. After 30 hours, complete conversion to the Re hydride *trans*-$(PPh_3)Re(CO)_4H$ [^{1}H NMR δ -4.65 (d, J_{PH} = 22.5 Hz); $^{31}P\{^1H\}$ NMR δ 15.7] was observed.

B. Reduction of [(Ph$_2$PCH$_2$B(C$_8$H$_{14}$))Re(CO)$_5$][OTf] ([1-M$_1$][OTf]).

Reaction of [1-M$_1$][OTf] with 1 equiv [HPt][PF$_6$].

A 20 mL scintillation vial was charged with 99.1 mg (0.124 mmol) [**1-M$_1$**][OTf] and 2 mL C_6H_5Cl. With rapid stirring, 79.8 mg (0.124 mmol) [**HPt**][PF_6] was added in ~10 mg portions slowly over ~5 minutes. The mixture was allowed to stir overnight, at which point it was filtered through celite (washing with 1 mL C_6H_5Cl and 2 mL pentane), and the solvents were removed under vacuum. The oily residue was triturated briefly with pentane and the solvents were again removed under vacuum. The white solids were extracted with 5 mL pentane, filtered, and the solvents removed under vacuum to give 70 mg (87%) ~95% pure **2-M$_1$**. The side product was a Re-C*H*$_2$-containing species (δ 5.18 d, J_{PH} = 6.3 Hz) which had spectral characteristics (^{31}P NMR, δ -8.9 (1P), 2.3 (1P)) similar to more completely characterized dirhenium alkyl-dioxycarbene species **10-E$_1$**. **^{1}H NMR** (C_6D_6, 300 MHz): δ 1.16 (br, 2H, $Ph_2PCH_2B(C_8H_{14})$), 1.3-1.8 (br, $Ph_2PCH_2B(C_8H_{14})$), 1.65 (d, J_{PH} = 12.9 Hz, $Ph_2PCH_2B(C_8H_{14})$), 2.02 (br, $Ph_2PCH_2B(C_8H_{14})$), 2.30

(br, $Ph_2PCH_2B(C_8H_{14})$; integration of all broad peaks from 1.3-2.6 is 16H as expected), 6.89-6.98 (m, 6H, $Ph_2PCH_2B(C_8H_{14})$), 7.25-7.32 (m, 4H, $Ph_2PCH_2B(C_8H_{14})$), 13.72 (d, JPH = 2.5 Hz, 1H, Re-C*H*O). **$^{31}P\{^1H\}$ NMR** (C_6D_6, 121 MHz): δ -0.2. **$^{13}C\{^1H\}$ NMR** (C_6D_6, 125 MHz): δ 14.76 (br), 25.41 (br), 26.90 (br), 31.54 (br), 32.49 (br), 128.77 (d, J_{PC} = 9.9 Hz), 130.31 (d, J_{PC} = 1.9 Hz), 132.02 (d, J_{PC} = 10.4 Hz), 137.75 (d, J_{PC} = 46.8 Hz), 186.93 (br, eq. COs), 189.80 (br, axial CO), 282.48 (br, Re-*C*HO). **^{11}B NMR** (C_6D_5Cl, 160 MHz): δ 11.2. **IR** (heptane): ν_{CO} 2096 (m), 2003 (s), 1975 (s), 1945 (m), ν_{CHO} 1517 cm^{-1}. **IR** (CH_2Cl_2): 2097 (m), 2000 (s), 1972 (s), 1942 (sh), 1507 cm^{-1}.

Variable temperature NMR experiments were undertaken as some of the $-B(C_8H_{14})$ resonances were broad. As the probe was cooled, the broad $-B(C_8H_{14})$ resonances sharpened significantly but otherwise remained relatively featureless. The carbene proton shifted slightly with temperature, although the coupling constant remained ~2 Hz at all temperatures. The broad ^{11}B NMR resonance disappeared at low temperatures. The broadening could be due to B-O de-coordination, as further evidenced by the reactivity of **2-M$_1$** with pyridine (see below).

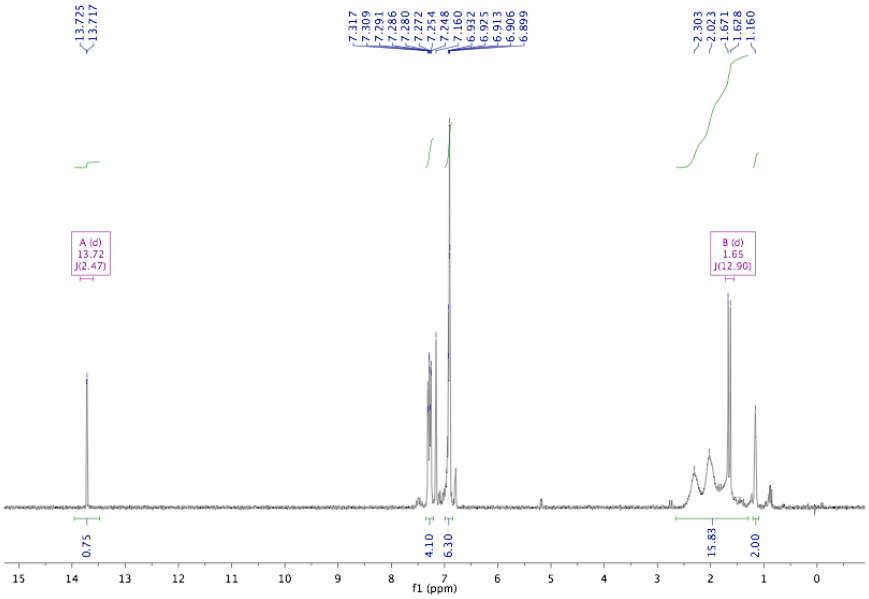


Figure S126. ^1H NMR.

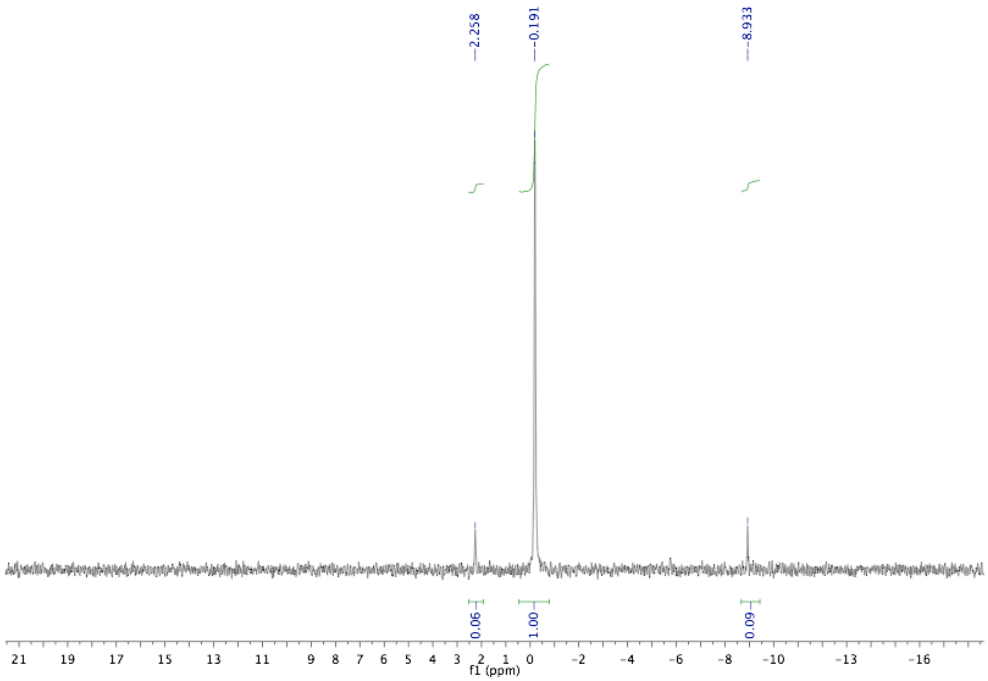


Figure S127. $^{31}P\{^{1}H\}$ NMR.

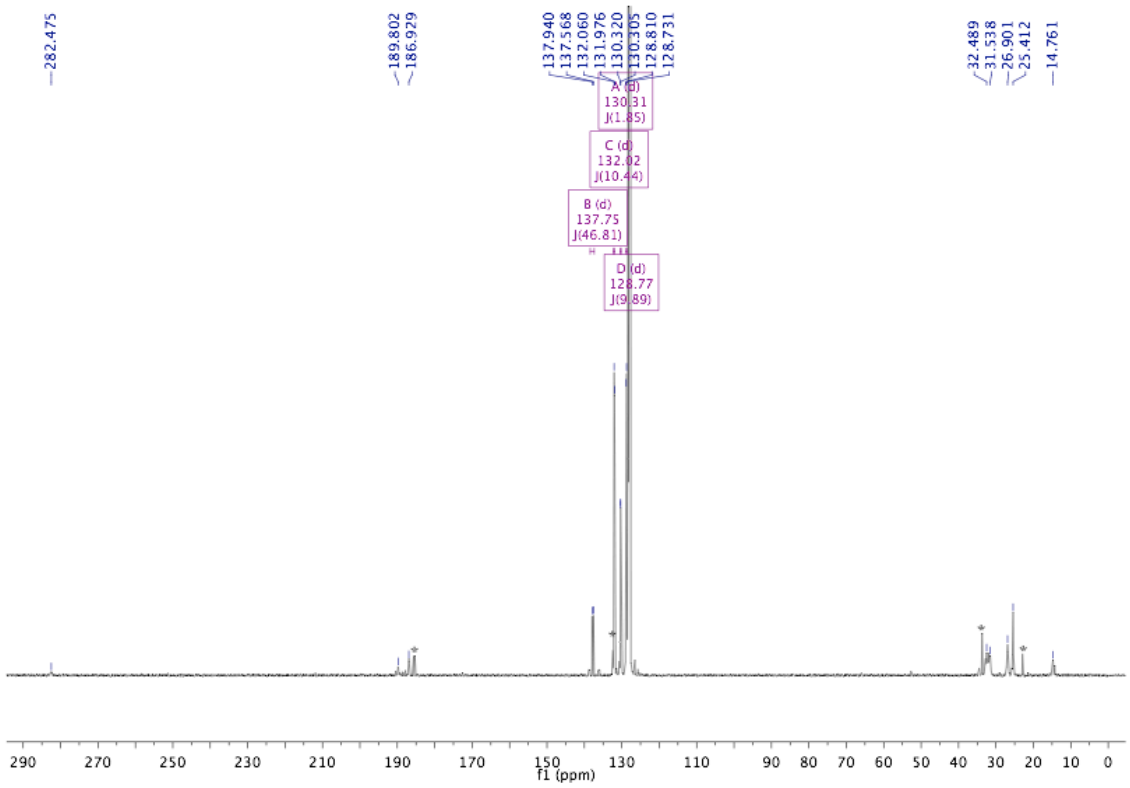


Figure S128. $^{13}C\{^{1}H\}$ NMR.

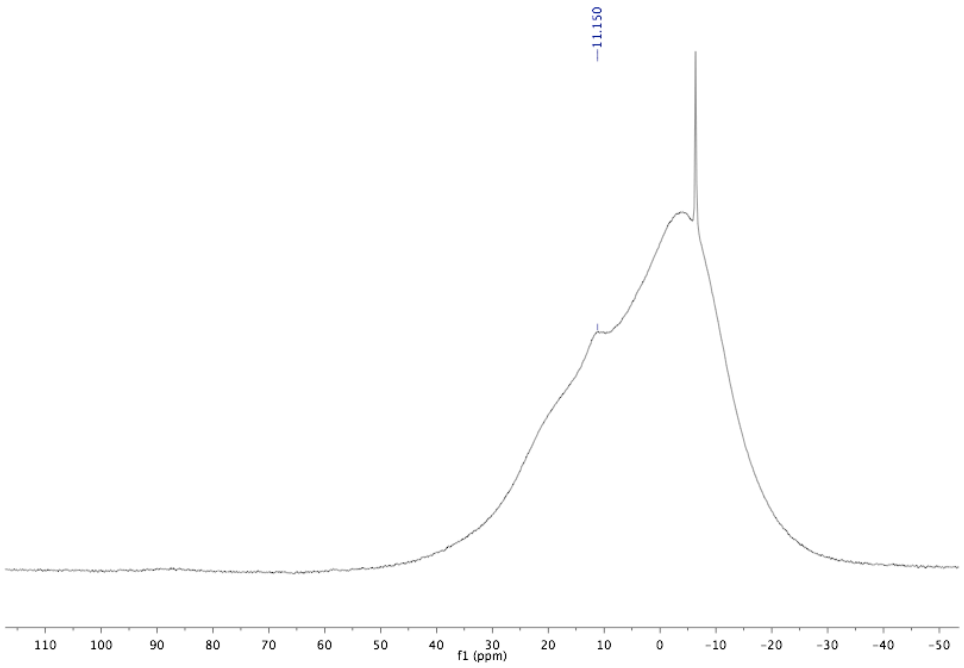


Figure S129. ^{11}B NMR.

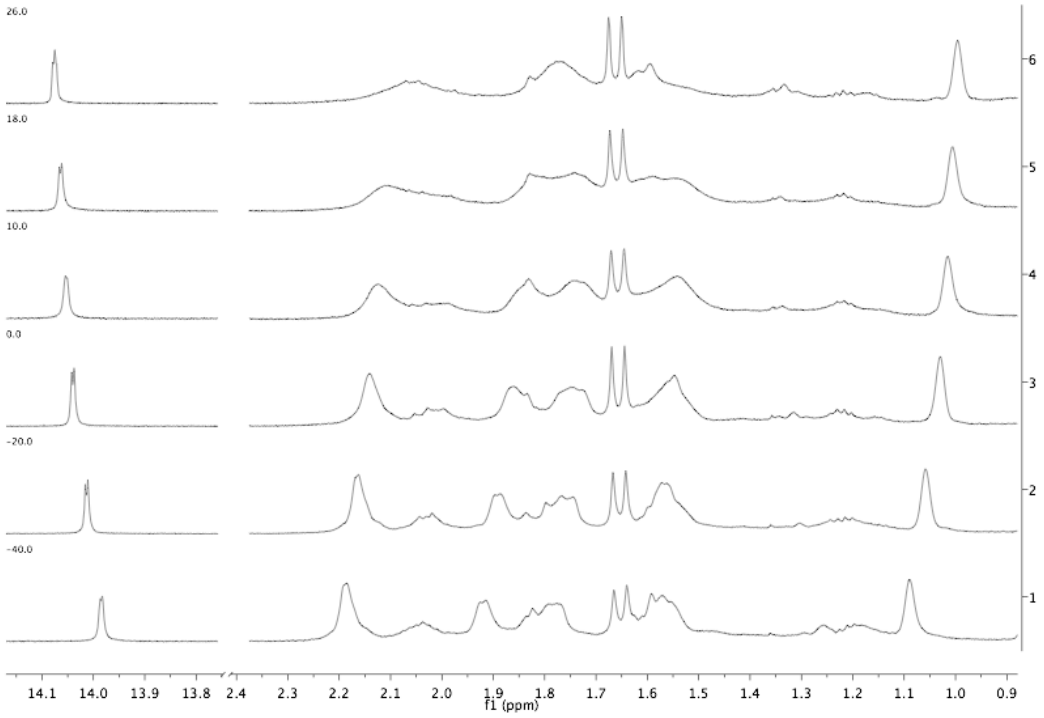


Figure S130. ^{1}H NMR (Variable temperature).

Decomposition of 2-M_1.

While searching for ideal conditions to reduce [**1-M_1**][OTf], a J-Young tube was charged with 19.3 mg (0.0242 mmol) [**1-M_1**][OTf], 4.0 mg (0.031 mmol) $NaHB(OMe)_3$, and ~0.6 mL C_6D_5Cl. The mixture turned yellow and was monitored by NMR spectroscopy, which showed conversion to two products in a ~2:1 ratio, with the major product being the boroxycarbene **2-M_1**. The product distribution was largely stable for weeks, but after 1 month NMR spectra showed nearly complete consumption of the carbene and formation of a new species containing three diagnostic multiplets at 3.94, 5.30, and 6.39. A separate reaction was carried out in C_6H_5Cl under similar conditions, from which the solvents were removed under vacuum, followed by extraction with pentane and crystallization from slow pentane evaporation. Crystals of **11** grew only after a few months, and turned out to be the decomposition product. Although the reaction was fairly clean, the undesired product was not isolated or purified, and was only characterized as a mixture in the NMR experiments and by X-Ray crystallography. Similar partial decomposition was observed in [**HPt**]$^+$ reductions. Partial NMR spectroscopic details: ^{1}H NMR (C_6D_5Cl, 500 MHz): 3.95 (ddd, J_{HH} = 8.7 Hz, 14.5 Hz, J_{PH} = 12.0 Hz, Ph_2PCH_2C(O-)(H)-Re), 5.30 (dt, J_{HH} = 8.6 Hz, J_{PH} = 14.5 Hz, Ph_2PCH_2C(O-)(H)-Re), 6.40 (td, J_{HH} = 8.7 Hz, J_{PH} = 5.5, Ph_2PCH_2C(O-)(*H*)-Re). $^{31}P\{^1H\}$ NMR (C_6D_5Cl, 121 MHz): -54.0 (1P), 1.8 (1P, 4-membered ring). $^{13}C\{^1H\}$ NMR (C_6D_5Cl, 75 MHz): 44.13 (J_{PC} = 6.3 Hz, Ph_2PCH_2C(O-)(*H*)-Re), 52.24 (J_{PC} = 39.3 Hz, Ph_2PCH_2C(O-)(H)-Re), 210.20 (d, J_{PC} = 9.4 Hz, Re=*C*(O-)O-C(R)H-Re).

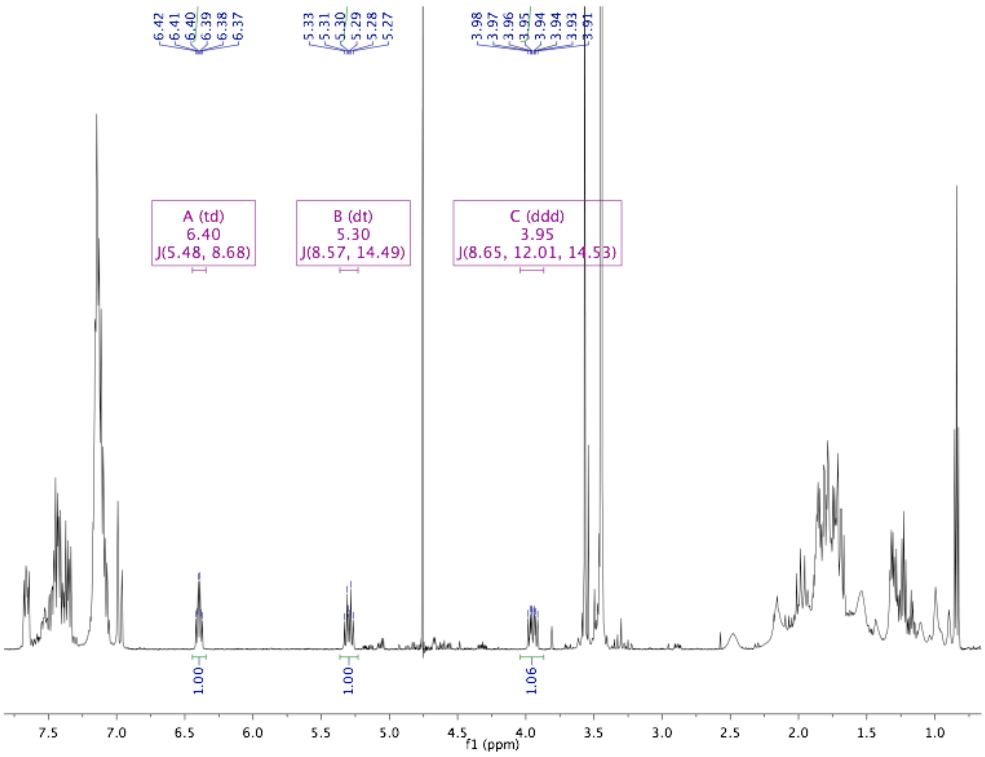


Figure S131. ^{1}H NMR.

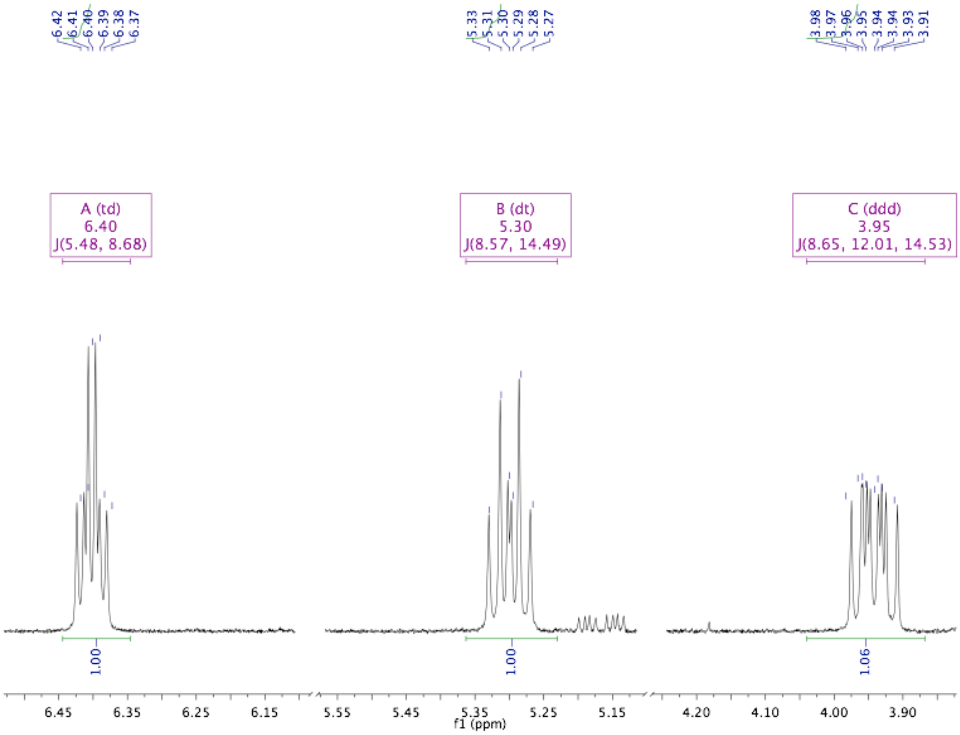


Figure S132. ^{1}H NMR (blow-up of cyclic alkyl region).

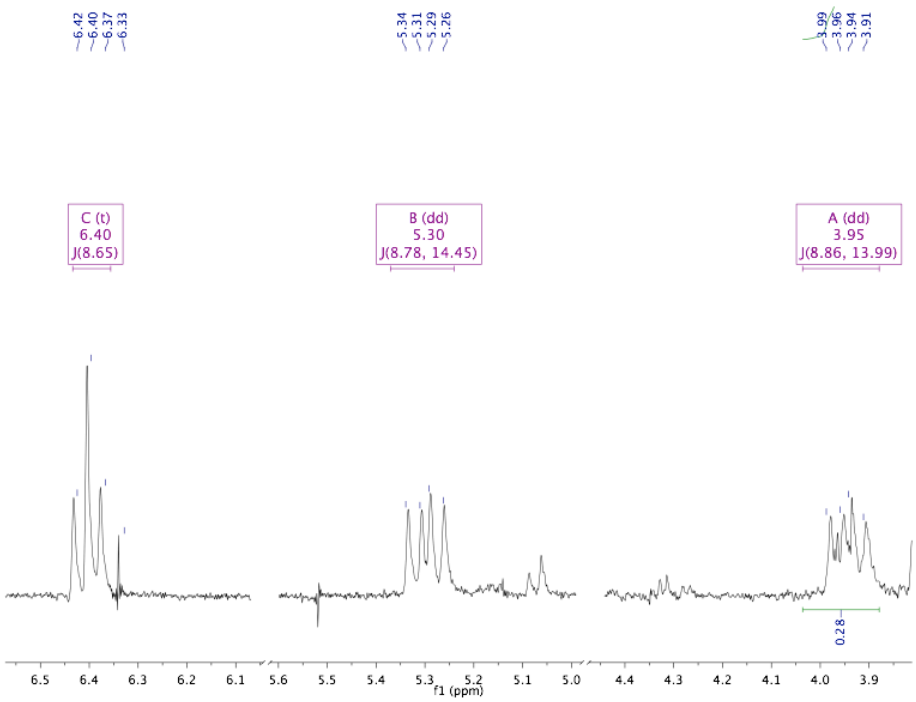


Figure S133. $^{1}H\{^{31}P\}$ NMR.

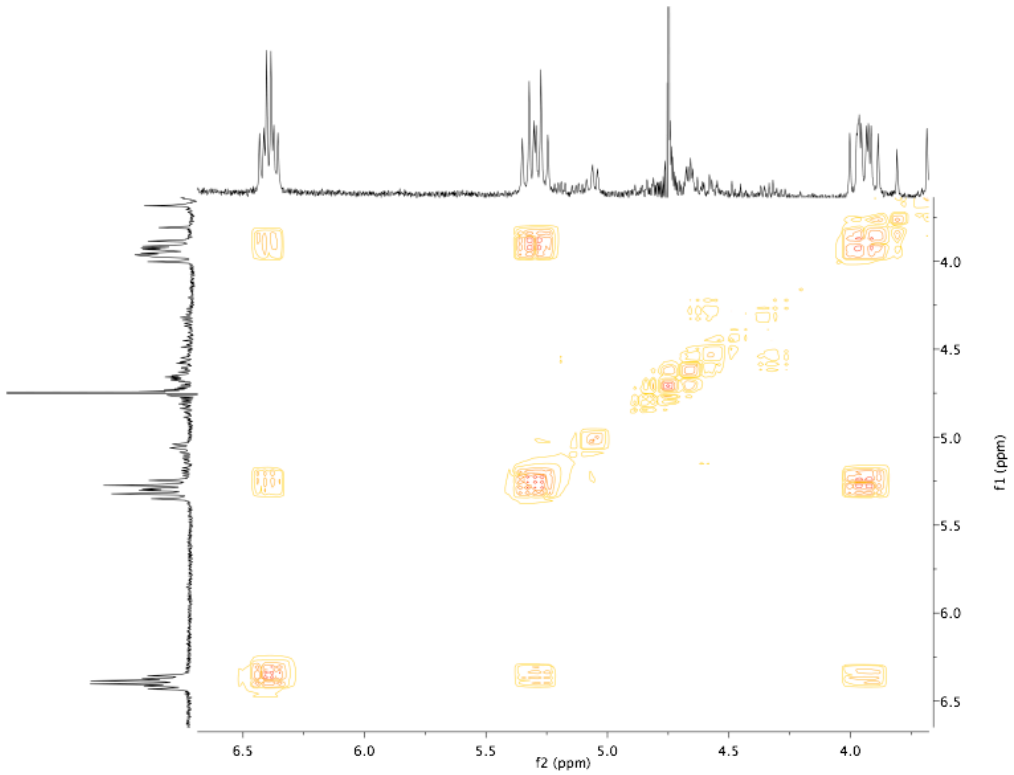


Figure S134. ^{1}H-^{1}H gCOSY.

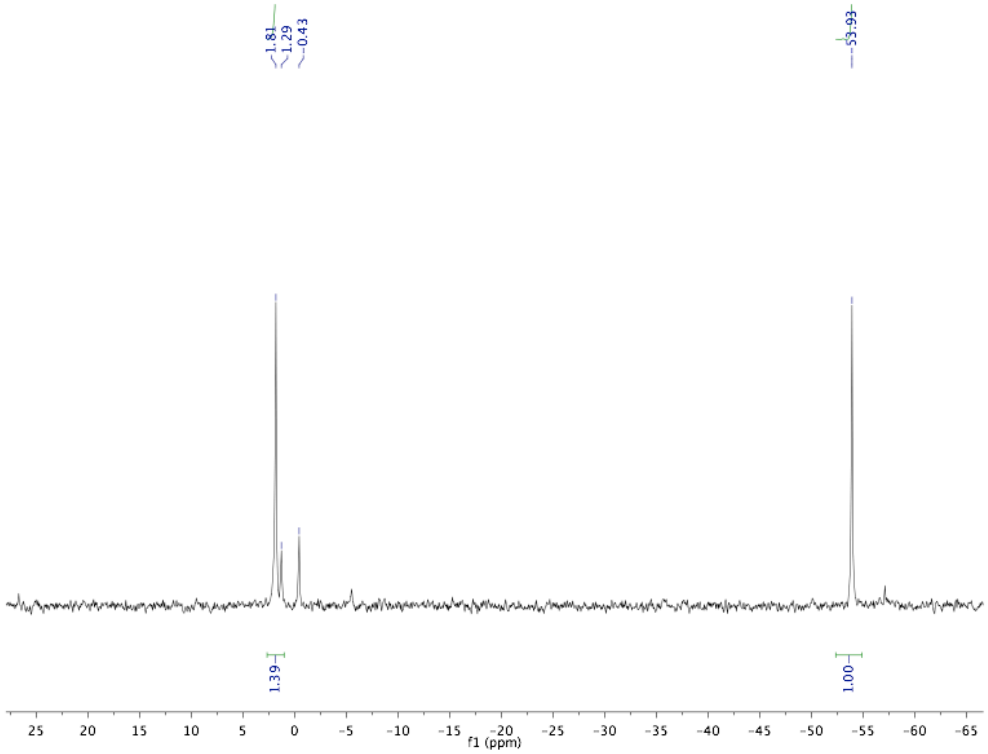


Figure S135. $^{31}P\{^{1}H\}$ NMR.

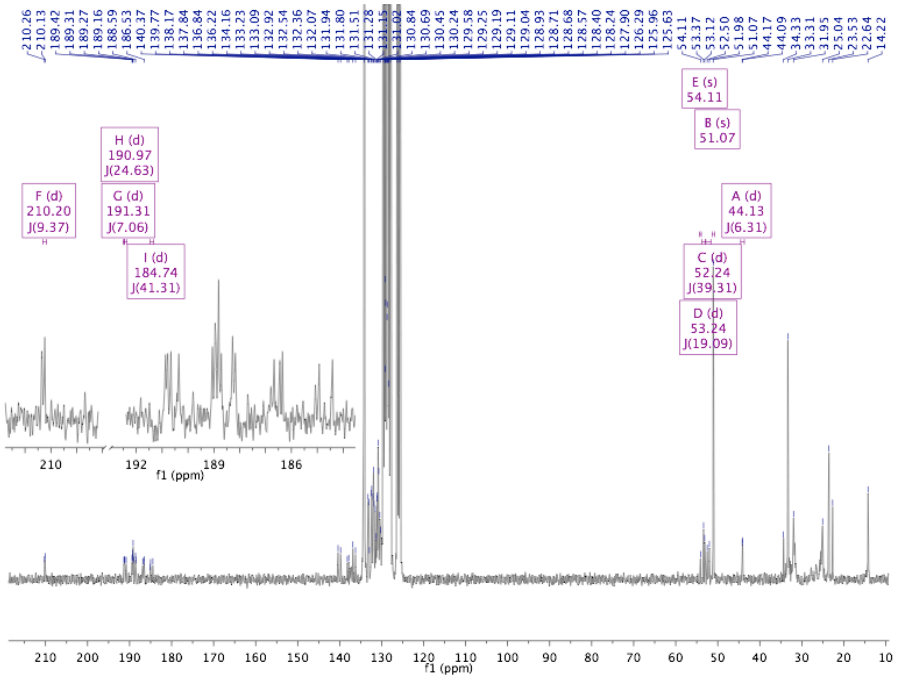


Figure S136. $^{13}C\{^{1}H\}$ NMR.

Reaction of [1-M_1][BAr^F_4] with [HPt][BAr^F_4]. Reaction of 2-M_1 with pyridine.

A small vial was charged with 38.0 mg (0.0254 mmol) [**1-M_1**][BAr^F_4] and ~0.6 mL C_6D_5Cl. With stirring, 34.5 mg (0.0254 mmol) [**HPt**][BAr^F_4] was added as a solid, and the mixture was transferred to a J-Young NMR tube and monitored by NMR spectroscopy. After about 30 minutes, only a small resonance for **2-M_1** was observed. The reaction slowly proceeded over ~24 hours, eventually consuming all [**HPt**]$^+$ and affording spectra matching previous syntheses of **2-M_1** (using OTf/PF_6 salts).

To the tube containing **2-M_1** was added 4 μL pyridine (0.0503 mmol, 2 equiv), and the tube was sealed and shaken to mix. NMR spectroscopy revealed consumption of the carbene with formation of a new bridging alkyl species. Multinuclear NMR spectroscopy was very similar to analytically characterized **10-E_1** (see below), confirming the analogous structure **10-M_1-py**. For **10-M_1-py**: **^{1}H NMR** (C_6D_6, 300 MHz): δ 0.92 (br, 2H, $Ph_2PCH_2B(C_8H_{14})$), 1.17 (br, 4H, $Ph_2PCH_2B(C_8H_{14})$), 1.71 (br m, 6H, $Ph_2PCH_2B(C_8H_{14})$), 1.81 (d, J_{PH} = 13.0 Hz, 2H $Ph_2PCH_2B(C_8H_{14})$), 1.9-2.2 (br m, 12H, $Ph_2PCH_2B(C_8H_{14})$), 2.32 (d, J_{PH} = 11.5 Hz, 2H, $Ph_2PCH_2B(C_8H_{14})$), 2.39 (br, 4H, $Ph_2PCH_2B(C_8H_{14})$), 5.05 (d, J_{PC} = 5.7 Hz, 2H, Re-CH_2O-), 6.22 (br, 2H, pyridine), 6.55 (br, 1H, pyridine), 6.9-7.0 (m, 12H, Ph), 7.31 (m, 4H, Ph), 7.48 (m, 4H, Ph), 7.72 (br, 2H, pyridine). **^{31}P{^{1}H} NMR** (C_6D_6, 121 MHz): δ -4.4 (1P), 2.4 (1P). **^{13}C{^{1}H} NMR** (C_6D_6, 126 MHz): 15.08 (d, J_{PC} = 11.8 Hz, $Ph_2PCH_2B(C_8H_{14})$), 24.41 ($Ph_2PCH_2B(C_8H_{14})$), 25.57 ($Ph_2PCH_2B(C_8H_{14})$), 26.22 (br, $Ph_2PCH_2B(C_8H_{14})$) 27.18 (d, J_{PC} = 10.6 Hz, $Ph_2PCH_2B(C_8H_{14})$), 30.45 ($Ph_2PCH_2B(C_8H_{14})$), 32.01 ($Ph_2PCH_2B(C_8H_{14})$), 32.85 ($Ph_2PCH_2B(C_8H_{14})$), 33.16 ($Ph_2PCH_2B(C_8H_{14})$), 54.39 (d, J_{PC} = 6.1 Hz, Re-CH_2O-C(O)-Re), 125.07 (pyridine), 128.34 (d, J_{PC} = 9.3 Hz, *m*-$Ph_2PCH_2B(C_8H_{14})$), 128.64 (d, J_{PC} = 9.8 Hz, *m*-$Ph_2PCH_2B(C_8H_{14})$), 129.85 (d, J_{PC} = 1.9 Hz, *p*-$Ph_2PCH_2B(C_8H_{14})$), 130.00 (d, J_{PC} = 2.1 Hz, *p*-

Ph$_2$PCH$_2$B(C$_8$H$_{14}$)), 132.35 (d, J_{PC} = 10.4 Hz, *o*-*Ph*$_2$PCH$_2$B(C$_8$H$_{14}$)), 132.47 (d, J_{PC} = 10.0 Hz, *o*-*Ph*$_2$PCH$_2$B(C$_8$H$_{14}$)), 137.36 (d, J_{PC} = 42.1 Hz, *ipso*-*Ph*$_2$PCH$_2$B(C$_8$H$_{14}$)), 138.77 (d, J_{PC} = 46.1 Hz, *ipso*-*Ph*$_2$PCH$_2$B(C$_8$H$_{14}$)), 139.39 (pyridine), 145.85 (pyridine), 184.89 (d, J_{PC} = 41.7 Hz, *C*O *trans* to P), 187.82 (d, J_{PC} = 8.5 Hz, 2 CO), 188.98 (d, J_{PC} = 45.5 Hz, CO *trans* to P), 189.41 (d, J_{PC} = 8.4 Hz, CO), 189.81 (d, J_{PC} = 6.7 Hz, CO), 191.08 (d, J_{PC} = 9.0 Hz, 2 CO), 211.60 (d, JPC = 9.4 Hz, Re-CH$_2$O-*C*(O)-Re). **IR** (C$_6$D$_6$): ν_{CO} 2095 (m), 2082 (m), 1997 (br s), 1960 (br s), 1935 (br s) cm^{-1}.

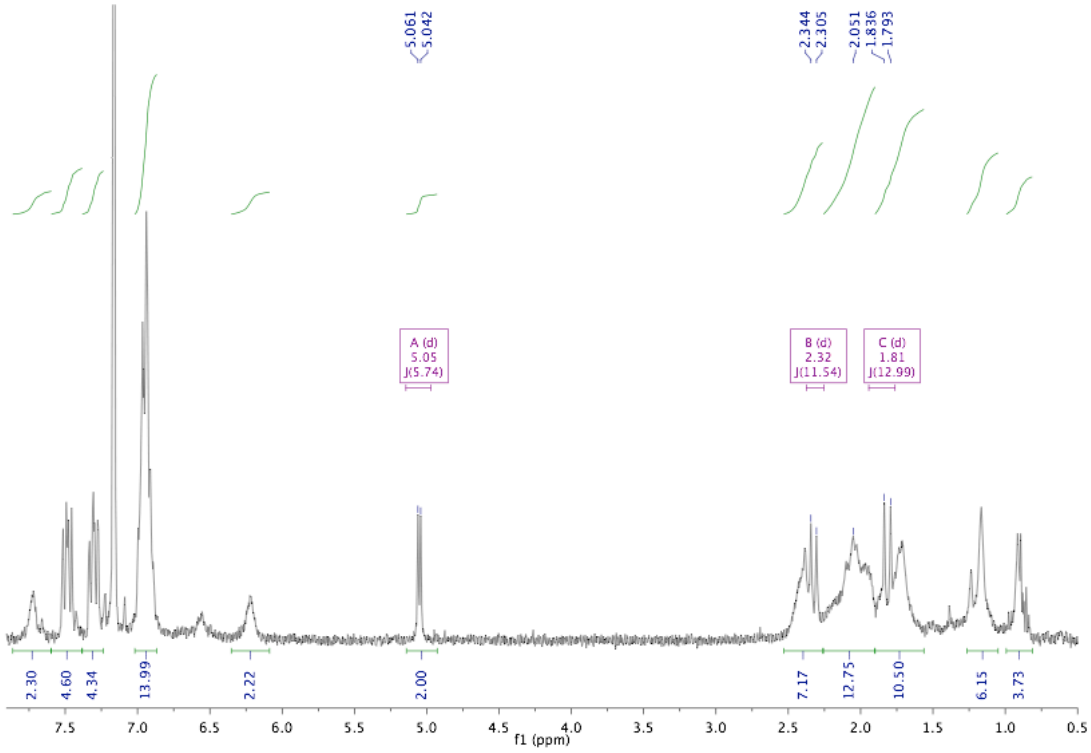


Figure S137. ^{1}H NMR.

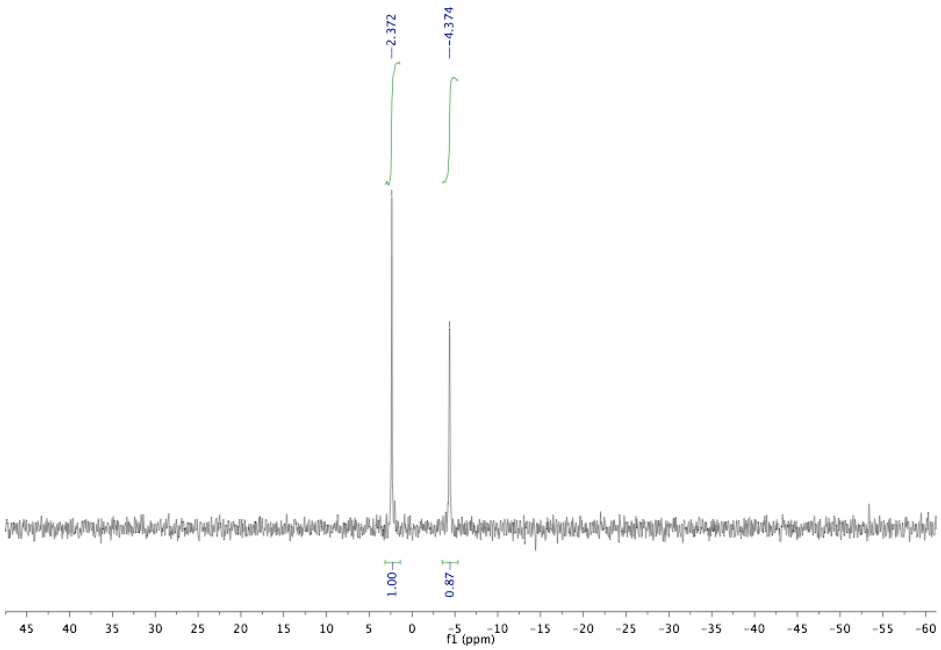


Figure S138. $^{31}P\{^{1}H\}$ NMR.

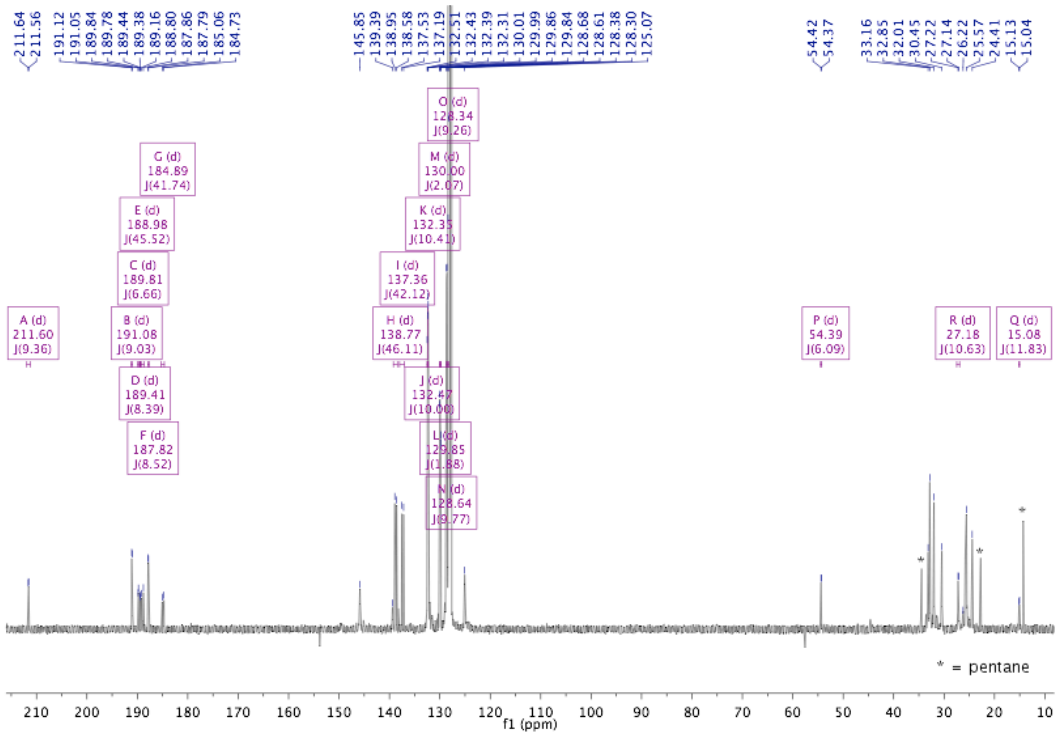


Figure S139. $^{13}C\{^{1}H\}$ NMR.

Reaction of 2-M_1 with 2-P_1 (Crossover Experiment).

To a stirring ~0.6 mL C_6D_5Cl solution of 19.3 mg (0.0240 mmol) [**1-M_1**][OTf] was added 15.6 mg (0.0240 mmol) [**HPt**]$^+$ partwise as a solid. The solution was transferred to a J-Young NMR tube, and showed ~90% conversion to **2-M_1** by NMR spectroscopy. The side product was the bridging alkyl as discussed in the synthesis of **2-M_1**. Meanwhile, **2-P_1** was prepared by addition of 15.6 mg (0.0240 mmol) solid [**HPt**]$^+$ to 20.0 mg (0.024 mmol) [**1-P_1**][OTf] with stirring. After one minute of stirring, the contents of the tube containing **2-M_1** were poured into the vial containing **2-P_1**, and the reaction mixture was filtered into a J-Young NMR tube. After ~20 minutes, a mixture of both Re-CHO species and a bridging alkyl-metalloester species were observed. After 3 hours, no Re-CHO species remained, and the major species (~90%) was identified by ^{1}H-^{31}P gHMBC NMR as **10-M_1P_1**, with the minor product being the initially formed impurity containing only 1C ligands. The 2-D NMR shows correlation of the CH_2 group to the ^{31}P signal at 0.1, which also correlates to two multiplets in the ^{1}H NMR at 2.46 and 1.56, belonging to the **P** ligand, and confirming that the CH_2 is bound the same metal as the **P** ligand. The other ^{31}P signal of the major species and the impurity overlap at 2.1 (the amount of impurity stayed roughly the same through the reaction). This resonance correlates to Ph protons and a doublet at 1.75, consistent with the other Re of both bimetallic species being ligated by **M**. As discussed in the text, this assignment allows for the mechanistic pathway of formation of the bridging alkyl to be identified as nucleophilic attack by oxygen.

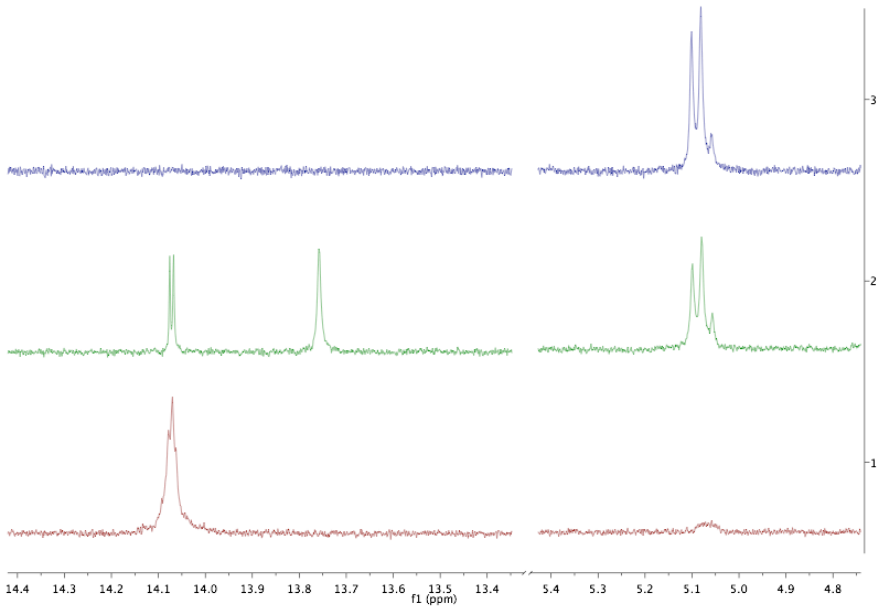


Figure S140. ^{1}H NMR time course. Bottom spectrum is **2-M$_1$** before addition of **2-P$_1$** (poor shimming due to solid Pt^{2+} salts formed during reaction). Middle spectrum is ~20 minutes after addition of **2-P$_1$** (after filtration). Top spectrum is upon completion of the reaction.

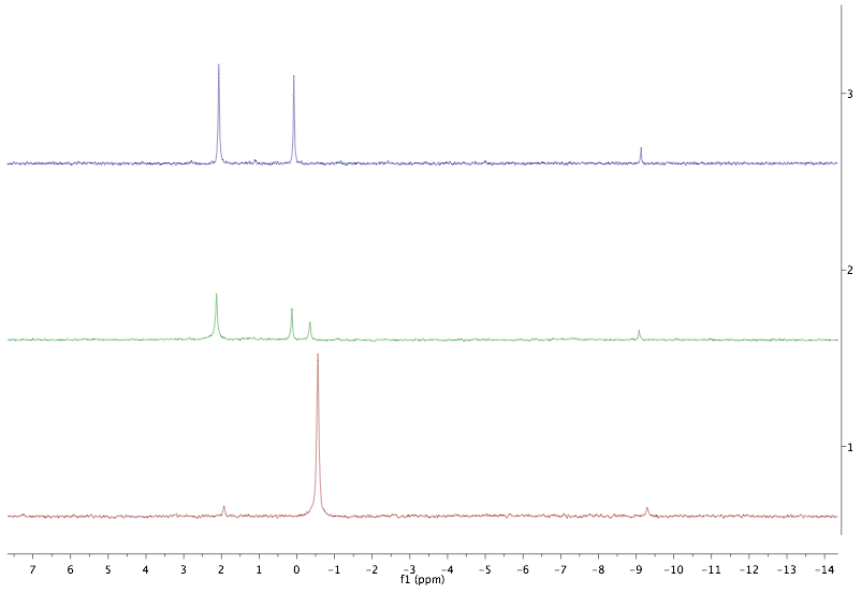


Figure S141. ^{1}H NMR time course. Bottom spectrum is **2-M$_1$** before addition of **2-P$_1$**. Middle spectrum is ~20 minutes after addition of **2-P$_1$** (after filtration). Top spectrum is upon completion of the reaction.

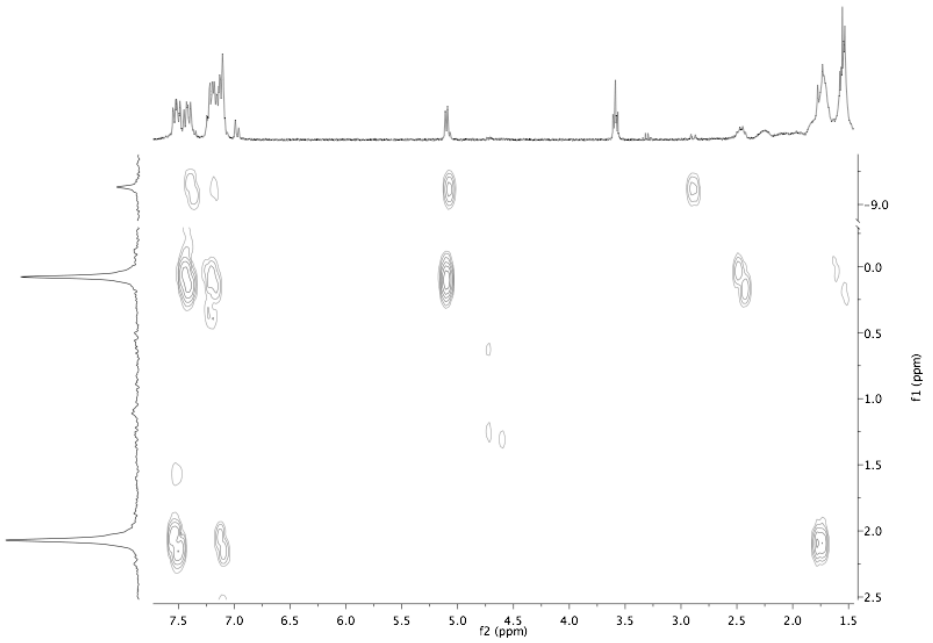


Figure S142. ^{1}H-^{31}P gHMBC NMR.

Reduction of [($Ph_2PCH_2B(C_8H_{14})$)$Re(CO)_5$][OTf] ([1-M_1][OTf]) with 2 equiv hydride.

A number of conditions, including changes in hydride source, solvent, anion, and countercation were varied. The results were generally similar; depending on the countercation of the product ([**HPt**]$^{+}$, [**Pt**]$^{2+}$, etc) the peaks shifted subtly, including the Re-C(O)CH_2O- group, the two doublets of which were sometimes more well resolved than others (moving to a singlet with Na^{+} present). Typical procedure using two equiv [**HPt**][PF_6]: to a stirring ~0.6 mL C_6D_5Cl solution of 26.5 mg (0.0333 mmol) [**1-M$_1$**][OTf] was added 21.3 mg (0.0333 mmol, 1 equiv) [**HPt**][PF_6] partwise as a solid. The reaction was allowed to stir for 15 minutes, at which point the reaction mixture was filtered into a small vial charged with another 21.3 mg (0.0333 mmol, 1 equiv) of [**HPt**][PF_6]. Despite measuring 1 equivalent of hydride, ~2 equiv was actually delivered, as the filtration left some carbene behind. The mixture was then transferred to a J-Young tube, and monitored by multinuclear NMR spectroscopy. After 20 minutes, carbene **2-M$_1$** was essentially

the only Re species, but after 2.5 hours a mixture of **2-M$_1$**, and two new species were observed, identified as Re alkyl **12** and the migratory insertion product [**3-M$_1$**]$^-$. After 2.5 hours, there was more alkyl **12** present than the final product (^{1}H NMR δ 5.14 (d, J_{PH} = 1.9 Hz); ^{31}P{^{1}H} NMR δ 3.4). After 24 hours, the starting carbene had been almost entirely consumed, and the major species was the acyl. After 48 hours, the reaction was complete, with only the acyl and residual [**HPt**]$^+$ remaining. 2D NMR experiments were performed on a reaction carried out in CD_2Cl_2, which contained a mixture of [**3-M$_1$**]$^-$, the alkyl intermediate **12**, and small amounts of bridging alkyl impurities. Details of the crucial correlations that led to the structural assignment of the products are supplied by the appropriate figures. Typical procedure using $NaHBEt_3$: To a stirring ~0.6 mL C_6D_5Cl solution of 21.1 mg (0.0265 mmol) [**1-M$_1$**][OTf] was added 17.0 mg (0.0265 mmol) [**HPt**][PF_6] slowly as a solid. The mixture turned yellow with precipitation while it was allowed to stir for 10 minutes. After 10 minutes, the mixture was filtered through sintered glass, and 26.5 μL $NaHBEt_3$ (1.0 M in toluene) was added dropwise. Use of the stronger hydride source led to a much faster reaction, with complete conversion to in 2.5 hours. The ^{1}H and ^{31}P resonances were at approximately the same chemical shift, but were dramatically broadened relative to the [**HPt**]$^+$ reactions. Addition of pyridine directly following $NaHBEt_3$ (in a separate experiment) led to a moderate decrease in reaction rate, and a sharpening of the signals, suggesting BEt_3 is leading to broadening, and perhaps rate enhancement. Single crystals suitable for X-Ray diffraction were grown from this latter experiment, from a THF/pentane mixture at -35 °C. Characterization of acyl product [**3-M$_1$**]$^-$: **^{1}H NMR** (mix of [**Pt**]$^{2+}$ and [**HPt**]$^+$ salts, which obscure some $Ph_2PCH_2B(C_8H_{14})$ resonances, THF-d_8, 600 MHz): δ 0.43 (br, 1H, $Ph_2PCH_2B(C_8H_{14})$), 0.63 (br, 1H, $Ph_2PCH_2B(C_8H_{14})$), 0.71 (dd, J_{PH} = 9.8 Hz, J_{HH} = 14.4 Hz, 1H, $Ph_2PCH_2B(C_8H_{14})$), 1.29 (m, 1H), 1.37-1.43 (m, 3H), 1.53 (m, 1H), 4.64 (dd, J_{PH} = 1.9 Hz, J_{HH} =

15.1 Hz, 1H, Re-C(O)CH_2O-), 4.71 (d, J_{HH} = 15.0 Hz, 1H, Re-C(O)CH_2O-), 7.17-7.25 (m, 4H, Ph), 7.30 (m, 2H, Ph), 7.69 (m, 2H, Ph), 7.75 (m, 2H, Ph). **^{31}P{^{1}H} NMR** (THF-d_8, 121 MHz): δ -5.9 (J_{PtP} = 2214 Hz, [**HPt**]$^+$), 34.9 (J_{PtP} = 2184 Hz, [**Pt**]$^{2+}$), 38.8 (s, Re). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 126 MHz): δ 13.79 (br, [Pt(Me_2PCH$_2$CH$_2$PMe_2)$_2$]$^{2+}$), 21.34 (m, [HPt(Me_2PCH$_2$CH$_2$PMe_2)$_2$]$^+$), 26.14 (Ph$_2$PCH$_2$B(C_8H$_{14}$)), 26.37 (br, overlapping (Ph$_2$PCH$_2$B(C_8H$_{14}$)), 28.41 (br, [Pt(Me$_2$PCH$_2$$CH_2PMe_2$)$_2$]$^{2+}$), 30.61 (Ph$_2PCH_2$B($C_8H_{14}$)), 32.21 (Ph$_2PCH_2$B($C_8H_{14}$)), 32.88(m, [HPt(Me$_2PCH_2$$CH_2PMe_2$)$_2$]$^+$), 33.78 (Ph$_2PCH_2$B($C_8H_{14}$)), 35.38 (Ph$_2PCH_2$B($C_8H_{14}$)), 102.67 (ReC(O)$CH_2$O-), 128.38 (d, J_{PC} = 9.4 Hz, *m*-*Ph*$_2$PCH$_2$B(C$_8$H$_{14}$)), 128.40 (d, J_{PC} = 9.3 Hz, *m*-*Ph*$_2$PCH$_2$B(C$_8$H$_{14}$)), 129.34 (d, J_{PC} = 1.5 Hz, *p*-*Ph*$_2$PCH$_2$B(C$_8$H$_{14}$), 129.53 (d, J_{PC} = 1.3 Hz, *p*-*Ph*$_2$PCH$_2$B(C$_8$H$_{14}$)), 132.63 (d, J_{PC} = 11.2 Hz, *o*-*Ph*$_2$PCH$_2$B(C$_8$H$_{14}$)), 133.49 (d, J_{PC} = 10.7 Hz, *o*-*Ph*$_2$PCH$_2$B(C$_8$H$_{14}$)), 139.78 (d, J_{PC} = 40.5 Hz, *ipso*-*Ph*$_2$PCH$_2$B(C$_8$H$_{14}$)), 141.17 (d, J_{PC} = 39.2 Hz, *ipso*-*Ph*$_2$PCH$_2$B(C$_8$H$_{14}$)), 200.79 (d, J_{PC} = 53.3 Hz, CO *trans* to P), 202.26 (d, J_{PC} = 7.6 Hz, CO), 203.87 (d, J_{PC} = 8.3 Hz, CO), 274.74 (d, J_{PC} = 12.0 Hz, ReC(O)CH$_2$O-). ^{11}B NMR (CD_2Cl_2, 160 MHz): δ 6.5 (br). **IR** (CH_2Cl_2): ν_{CO} 1997 (s), 1906 (s), 1861 (s), $\nu_{C=O}$ 1615 (m). **HRMS (TOF MS ES$^-$):** Calcd for $C_{26}H_{28}BO_5PRe$, 649.1311. Found, 649.1325.

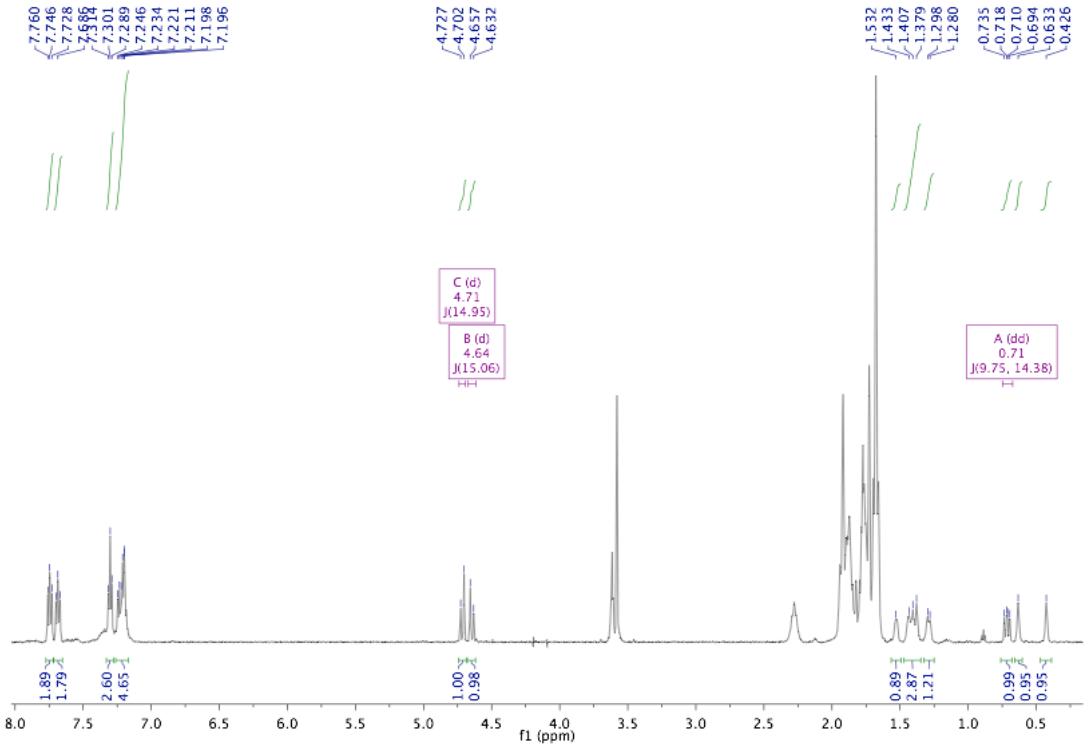


Figure S143. ^{1}H NMR.

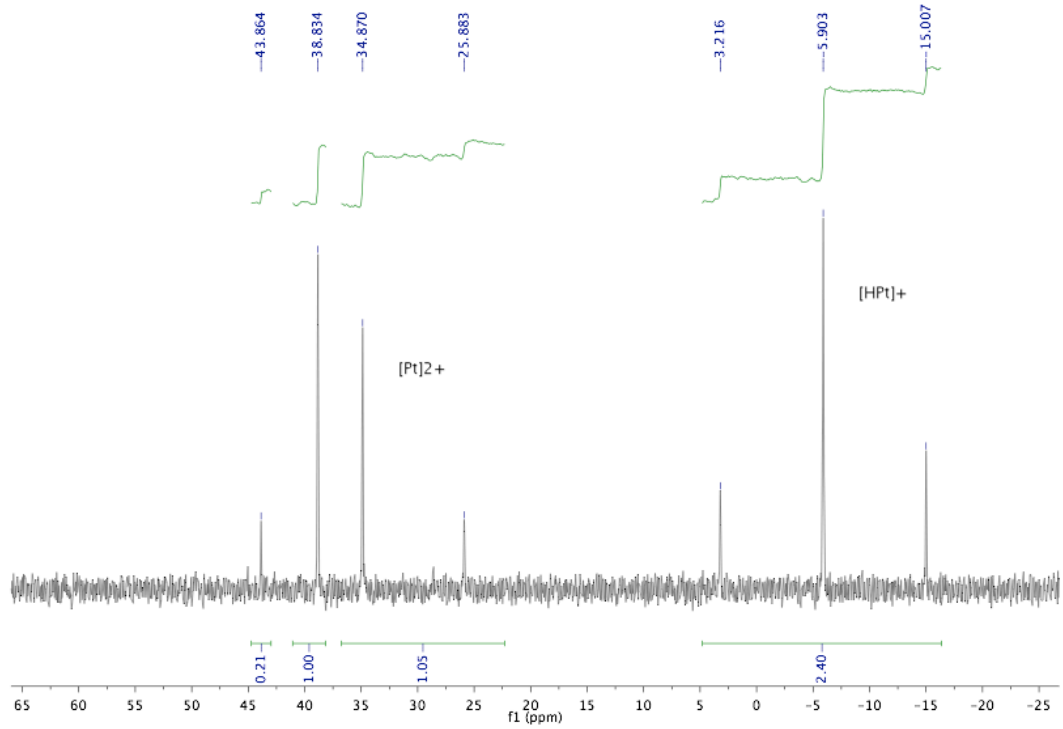


Figure S144. ^{31}P{^{1}H} NMR.

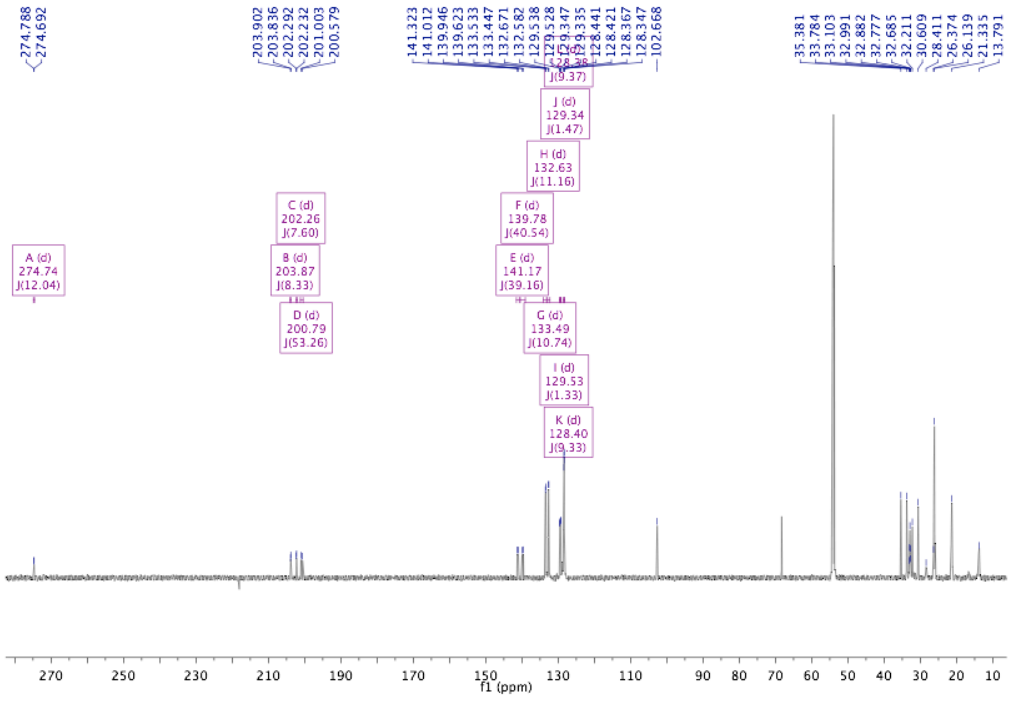


Figure S145. $^{13}C\{^{1}H\}$ NMR.

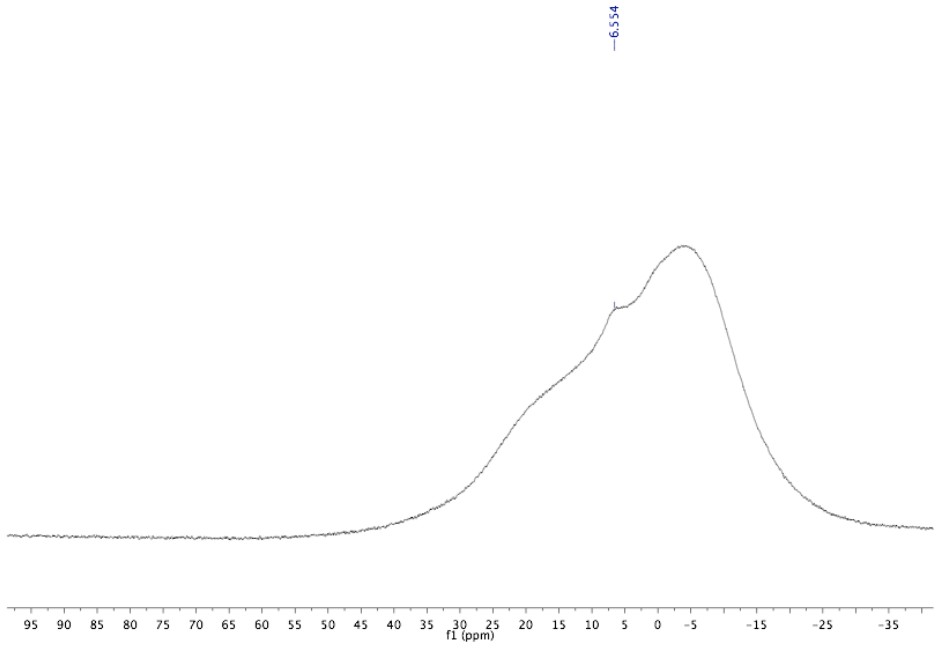


Figure S146. ^{11}B NMR.

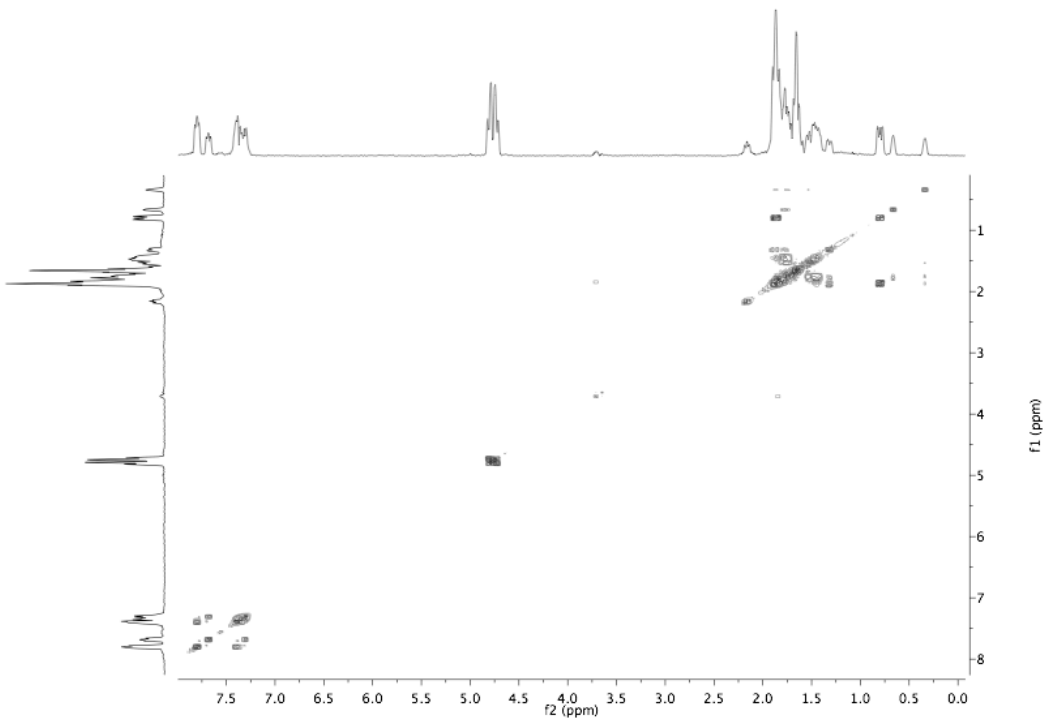


Figure S147. ^{1}H-^{1}H gCOSY.

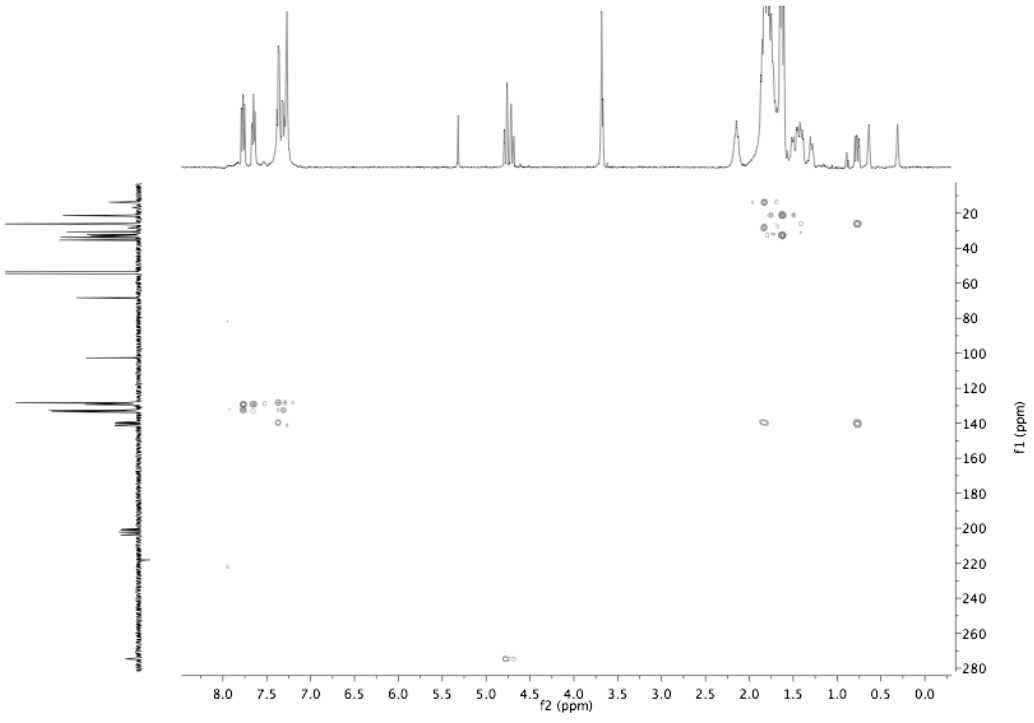


Figure S148. ^{1}H-^{13}C gHMBC.

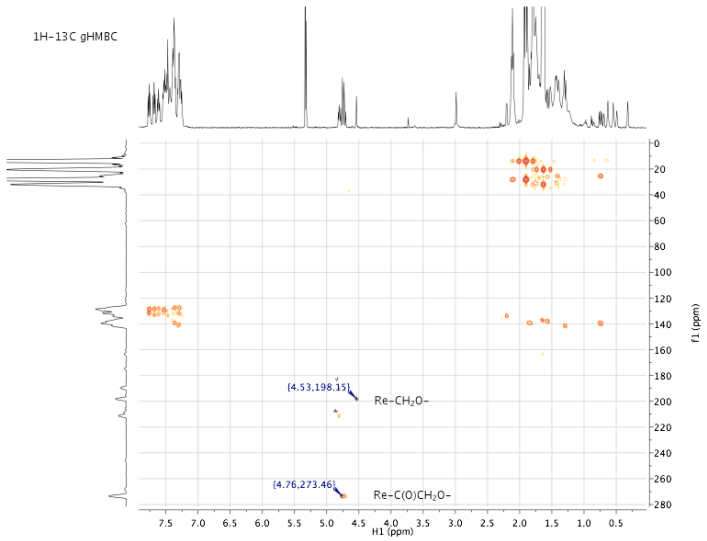


Figure S149. ^{1}H-^{13}C gHMBC (mixture of **12**, [**3-M$_1$**]$^-$; bridging alkyl impurity marked with star). The CH_2 group of **12** correlated through Re to a CO; [**3-M$_1$**]$^-$ is identified by the 2-bond coupling between Re-C(O)C*H*$_2$O- and Re-*C*(O)CH$_2$O-.

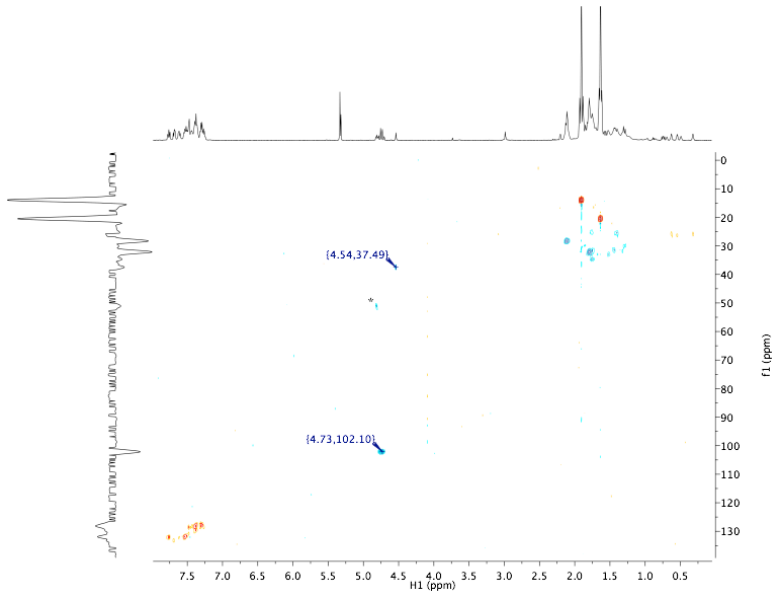


Figure S150. ^{1}H-^{13}C gHSQC (mixture of **12**, [**3-M$_1$**]$^-$; bridging alkyl impurity marked with star). The CH_2 group of [**3-M$_1$**]$^-$ correlates to a carbon near 100 ppm, close to that in [**3-E$_2$**]$^-$.

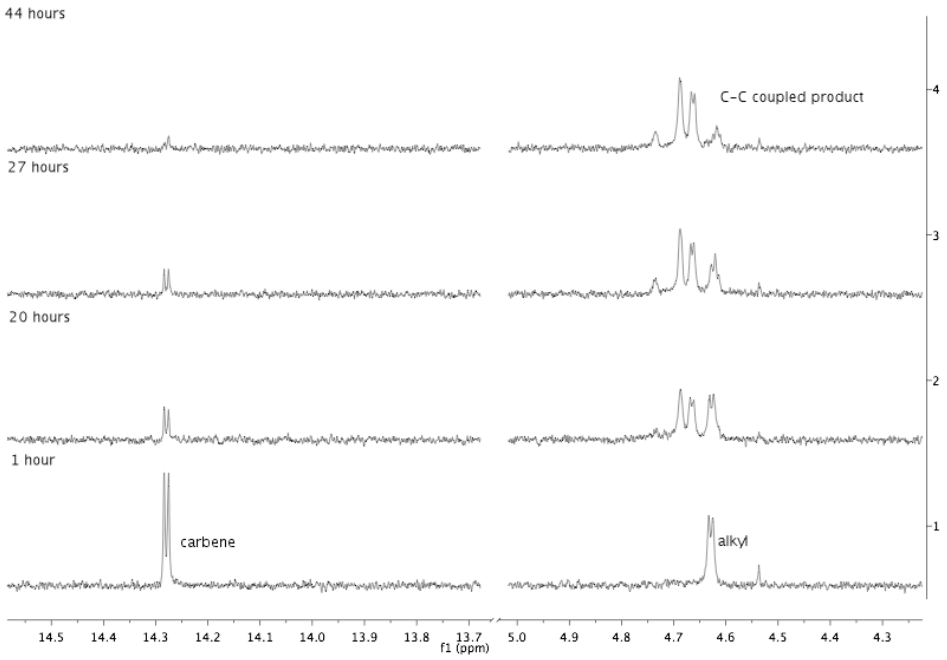


Figure S151. Reaction time course (2 equiv [**HPt**]$^+$ in THF-d_8).

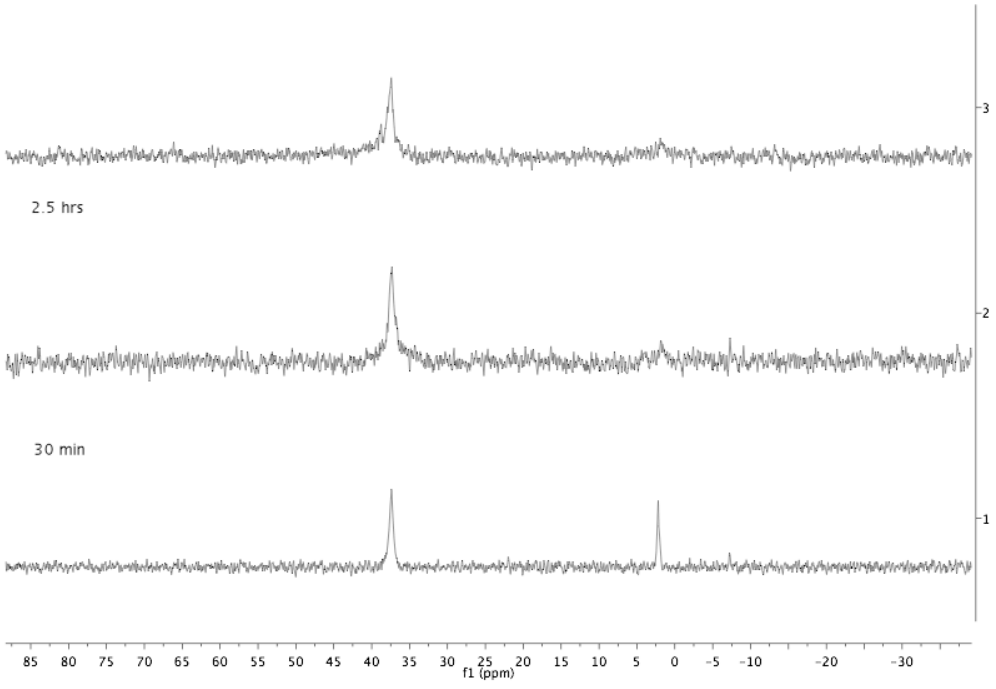


Figure S152. Reaction time course (1 equiv [**HPt**]$^+$, 1 equiv $NaHBEt_3$).

C. Reductions of [($Ph_2P(CH_2)_2B(C_8H_{14})$)$Re(CO)_5$][OTf] ([1-$E_1$][OTf]).

Reaction of [($Ph_2P(CH_2)_2B(C_8H_{14})$)$Re(CO)_5$][OTf] ([1-$E_1$][OTf]) with [HPt][$PF_6$].

To a stirring solution of 27.5 mg (0.034 mmol) [**1-E_1**][OTf] in ~0.6 mL C_6D_5Cl was added 24.0 mg (0.037 mmol) [$HPt(dmpe)_2$][PF_6] as a solid in small portions. After stirring for a minute, the reaction mixture was added to a J-Young NMR tube. After 20 minutes, essentially quantitative conversion to a new species was observed, identified as dinuclear bridging alkyl-dioxycarbene **10-E_1**. Filtration followed by removal of solvents gave analytically pure white solids. **^{1}H NMR** (600 MHz, C_6D_5Cl): δ 1.04-1.11 (m, 4H, $Ph_2PCH_2CH_2B(C_8H_{14})$), 1.21 (br, 2H, $Ph_2PCH_2CH_2B(C_8H_{14})$), 1.41 (m, 2H, $Ph_2PCH_2CH_2B(C_8H_{14})$), 1.53-1.58 (m, 6H, $Ph_2PCH_2CH_2B(C_8H_{14})$), 1.65 (br, 2H, $Ph_2PCH_2CH_2B(C_8H_{14})$), 1.70-1.77 (m, 6H, $Ph_2PCH_2CH_2B(C_8H_{14})$), 1.90 (m, 4H, $Ph_2PCH_2CH_2B(C_8H_{14})$), 2.11 (m, 6H, $Ph_2PCH_2CH_2B(C_8H_{14})$), 2.54 (m, 2H, $Ph_2PCH_2CH_2B(C_8H_{14})$), 2.73 (m, 2H, $Ph_2PCH_2CH_2B(C_8H_{14})$), 5.05 (d, J_{PH} = 6.9 Hz, 2H, Re-CH_2O-), 7.14-7.20 (m, 8H, $Ph_2PCH_2CH_2B(C_8H_{14})$), 7.24 (m, 4H, $Ph_2PCH_2CH_2B(C_8H_{14})$), 7.45 (m, 8H, $Ph_2PCH_2CH_2B(C_8H_{14})$). **^{31}P{^{1}H} NMR** (C_6D_5Cl, 121 MHz): δ 3.7 (1P), 13.3 (1P). **^{13}C{^{1}H} NMR** (C_6D_5Cl, 125 MHz): 13.95 (br, $Ph_2PCH_2CH_2B(C_8H_{14})$), 20.59 (br, $Ph_2PCH_2CH_2B(C_8H_{14})$), 23.16 ($Ph_2PCH_2CH_2B(C_8H_{14})$), 23.91 (d, J_{PC} = 17.4 Hz, $Ph_2PCH_2CH_2B(C_8H_{14})$), 25.39 ($Ph_2PCH_2CH_2B(C_8H_{14})$), 25.87 (d, J_{PC} = 27.8 Hz, $Ph_2PCH_2CH_2B(C_8H_{14})$), 26.97 (br, $Ph_2PCH_2CH_2B(C_8H_{14})$), 31.34 (br, $Ph_2PCH_2CH_2B(C_8H_{14})$), 32.78 ($Ph_2PCH_2CH_2B(C_8H_{14})$), 33.21 ($Ph_2PCH_2CH_2B(C_8H_{14})$), 49.88 (d, J_{PC} = 6.6 Hz, Re-CH_2O-), 128.69 (d, JPC = 9.6 Hz, Ph), 130.51 (d, J_{PC} = 24.9 Hz), 132.17 (d, J_{PC} = 9.6 Hz), 132.21 (d, J_{PC} = 9.6 Hz), 133.49 (d, J_{PC} = 44.9 Hz), 135.59 (d, J_{PC} = 46.3 Hz), 184.98 (d, J_{PC} = 44.0 Hz, CO), 187.23 (d, J_{PC} = 8.4 Hz, CO), 187.68 (d, J_{PC} = 6.9 Hz, CO), 187.69 (d, J_{PC} = 7.6 Hz, CO; overlap with preceding peak leads to

one broad doublet), 188.27 (d, J_{PC} = 48.2 Hz, CO), 189.94 (d, J_{PC} = 9.4 Hz, CO), 209.61 (d, J_{PC} = 10.5 Hz, Re-*C*(O-BR_3)OCH_2-). **IR** (C_6D_5Cl): υ_{CO}, 2090 (w), 2084 (w), 2013 (s), 1997 (s), 1965 (s), 1939 (s) cm^{-1}. **Anal. Calcd.** for $C_{54}H_{58}B_2O_{10}P_2Re_2$: C, 49.02; H, 4.42. Found: C, 48.74; H, 4.32.

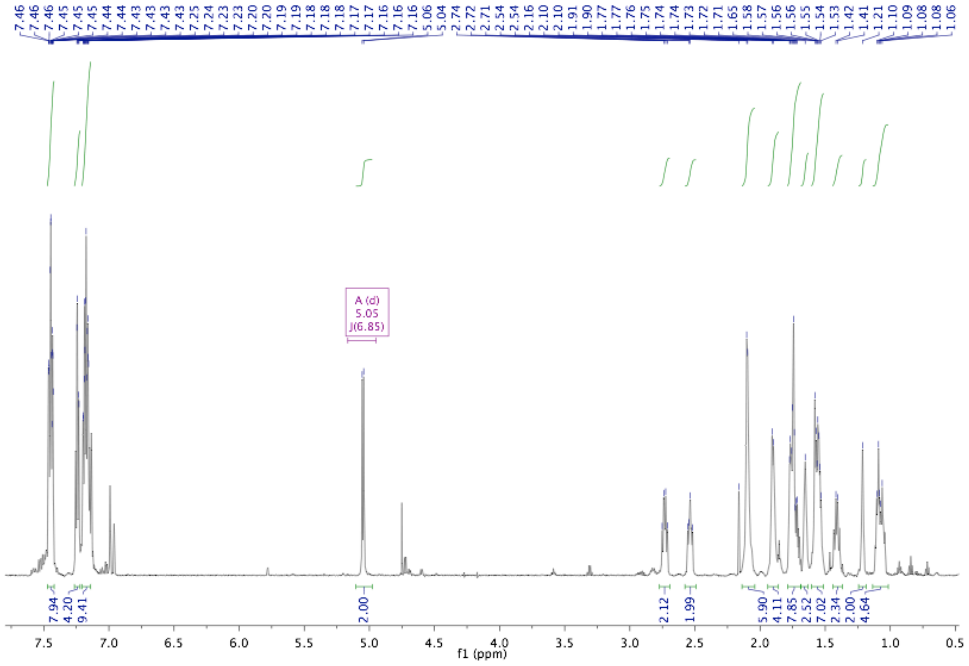


Figure S153. ^1H NMR.

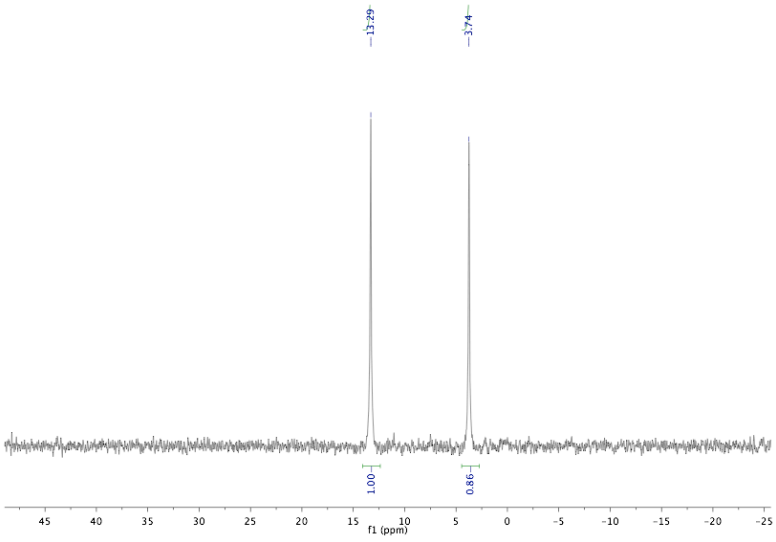


Figure S154. $^{31}P\{^1H\}$ NMR.

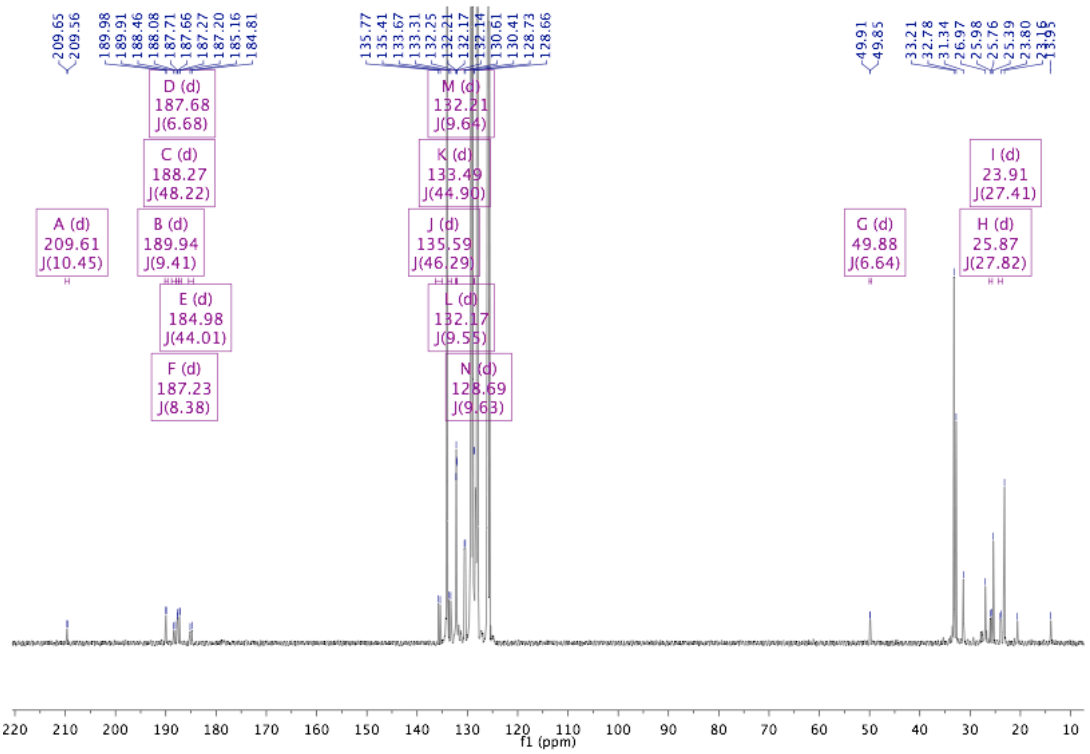


Figure S155. $^{13}C\{^{1}H\}$ NMR.

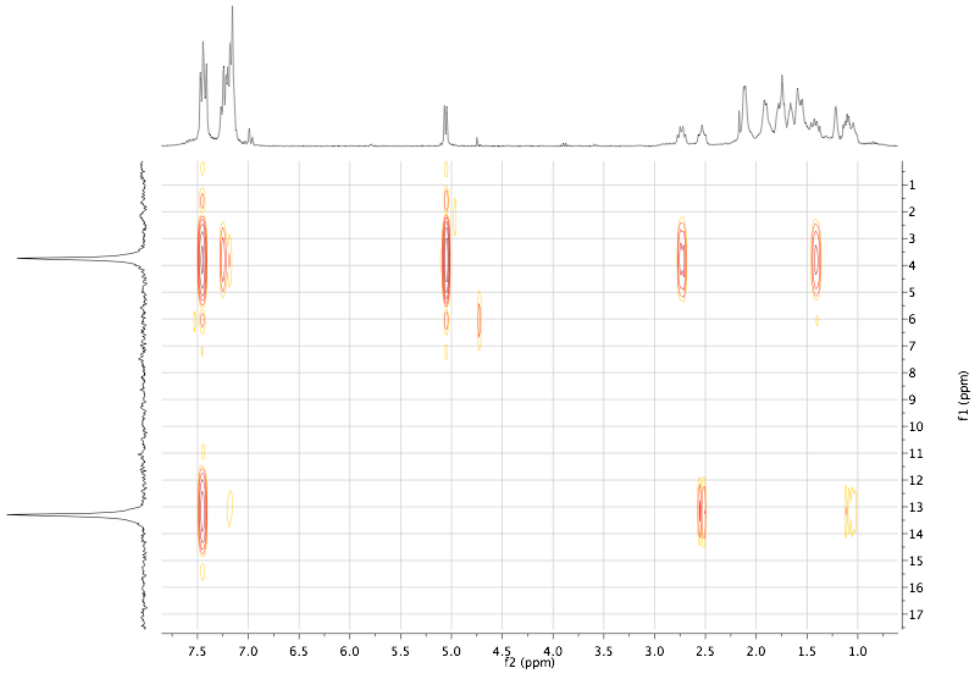


Figure S156. ^{1}H-^{31}P gHMBC.

Low temperature monitoring of the reaction of [1-E_1][OTf] with [HPt][PF_6].

A J-Young tube was charged with 25.8 mg (0.0318 mmol) cation [**1-E_1**][OTf]. Roughly 0.1 mL C_6D_5Cl was added, dissolving the cation. The tube was placed in a cold well chilled with liquid nitrogen, freezing the solution. A small amount of C_6D_5Cl was layered atop the frozen solution as a buffer, and the contents again were frozen. Roughly 0.3 mL of a C_6D_5Cl solution of 20.4 mg (0.0318 mmol) [**HPt**][PF_6] was added to the tube, which was then sealed and the contents frozen again. The tube was then removed from the box and the contents kept frozen in a dry ice/ acetone bath. At the NMR spectrometer, the tube was removed from the bath, and warmed until just thawing, at which point it was vigorously shaken and inserted into the probe (held at 25 °C). NMR spectra were acquired over ~30 minutes. Initial, spectra showed a mixture of starting materials and a carbene. Shortly thereafter the starting materials were consumed and a mixture of the carbene intermediate and the final alkyl product were observed. Over a few minutes at room temperature the carbene disappears, giving way to alkyl species **10-E_1** as the only observed product, as monitored by $^{31}P\{^1H\}$ NMR. For **2-E_1**: **^{1}H NMR** (C_6D_5Cl, 500 MHz -40 °C): δ 0.66 (br), 0.96 (br), 1.32 (br), 1.5-2.1 (br m), 2.32 (br), 7.00 (br), 7.1-7.3 (br m), 7.52 (br), 13.75 (br, Re-C*H*O). **$^{31}P\{^1H\}$ NMR** (C_6D_5Cl, 202 MHz, -40 °C): δ 7.4 (s).

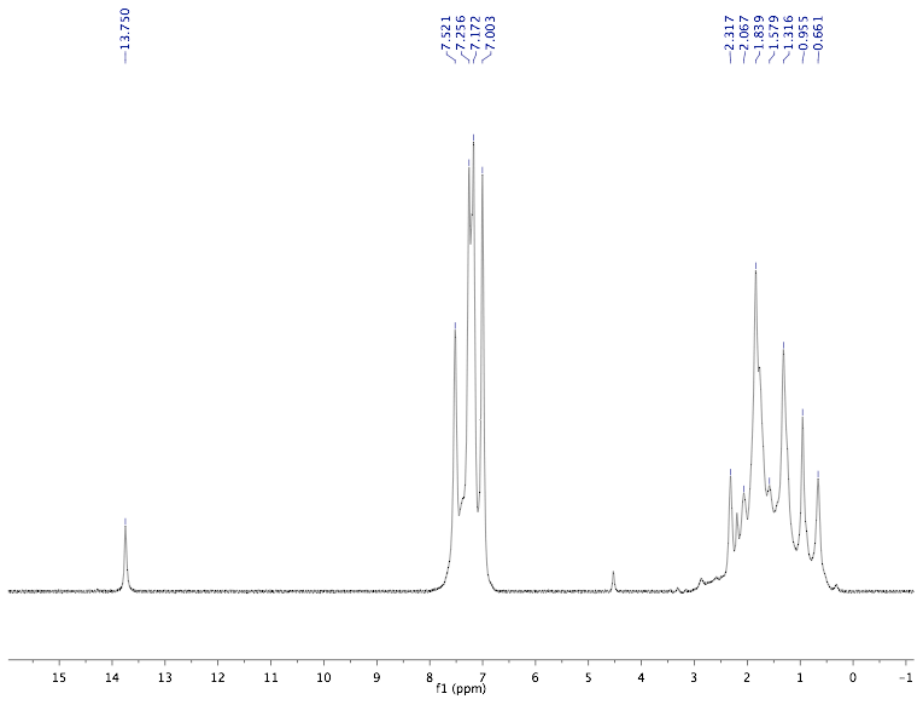


Figure S157. ^{1}H NMR (-40 °C).

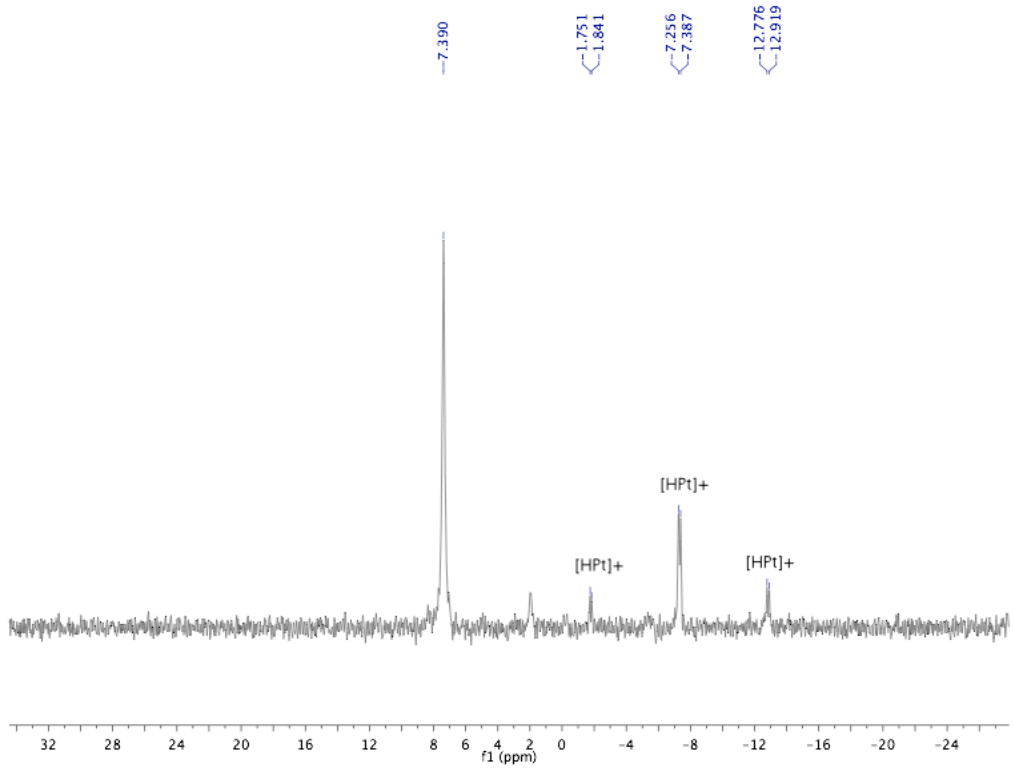


Figure S158. ^{31}P NMR (-40 °C).

D. Reductions of *trans*-[$(PPh_3)(Ph_2P(CH_2)_2B(C_8H_{14}))Re(CO)_4$][OTf] ([1-$E_1Ph_1$][OTf]).

Reaction of *trans*-[$(PPh_3)(Ph_2P(CH_2)_2B(C_8H_{14}))Re(CO)_4$][OTf] ([1-$E_1Ph_1$][OTf]) with 1 equiv $NaHBEt_3$.

Attempts to monitor the reduction of [**1-E_1Ph_1**][OTf] by a single hydride were thwarted by the precipitation of the product only a few minutes after reaction. A vial charged with 23.7 mg (0.0227 mmol) [**1-E_1Ph_1**][OTf] and ~0.6 mL THF-d_8 was stirred rapidly, and 22.7 μL $NaHBEt_3$ (1.0 M in toluene) was added dropwise. After ~10 minutes, significant precipitates had formed, and NMR spectroscopy revealed a mixture of boroxycarbene [^{1}H δ 13.42, ^{31}P{^{1}H} δ 9.3 (J_{PP} = 97 Hz) and 15.4 (J_{PP} = 97 Hz)] and Re-H (-4.94, d, J_{PH} = 22.6 Hz). The large coupling constant of the Re-H signal suggests it *trans*-$(PPh_3)Re(CO)_4H$, probably formed from a small amount of *trans*-$Re(CO)_4I$ remaining from the synthesis of [**1-E_1Ph_1**][OTf] (and not from decarbonylation, which would give a *cis*-hydride exclusively). No further reduction products were observed before complete precipitation of the boroxycarbene, suggesting that disproportionation is at least slower than precipitation in THF (significant disproporationation of **2-E_2** is observed in 15 minutes in THF).

Reaction of *trans*-[$(PPh_3)(Ph_2P(CH_2)_2B(C_8H_{14}))Re(CO)_4$][OTf] ([1-$E_1Ph_1$][OTf]) with 2 equiv $NaHBEt_3$.

0.130 g (0.125 mmol) [**1-E_1Ph_1**][OTf] was dissolved in 2 mL THF with stirring. To the rapidly stirring clear colorless solution was added dropwise 250 μL $NaHBEt_3$ (1.0 M in toluene). The solution turned bright yellow as the addition proceeded. The mixture was allowed to stir for 17 hours (note: NMR scale reactions showed the reaction is complete within minutes), after which

time the solvents were removed. A small amount (<1 mL) of benzene was added to the oily residues before drying again. The crude mixture was washed with benzene, and extracted with THF. Removal of the THF filtrate *in vacuo* yielded 0.098 g (0.1 mmol, 85%) C-C coupled acyl anion [**3-E$_1$Ph$_1$**]$^-$. Analytically pure single crystals suitable for X-Ray diffraction were grown from vapor diffusion of pentane into a THF solution of [Na][**3-E$_1$Ph$_1$**]. **^{1}H NMR** (THF-d_8, 600 MHz): δ 0.19 (1H), 0.69 (q, J_{PH} = 13.7 Hz, 1H), 1.12 (m, 2H), 1.4 (m, 2H), 1.5 (m, 2H), 1.53 (m, 1H), 1.64 (m, 1H), 1.7-1.9 (m, 5H), 2.1 (m, 1H), 2.71 (br t, J_{PH} = 14.0 Hz, 1H), 3.1 (m, 1H), 3.86 (d, $^2J_{HH}$ = 15.3 Hz), 4.10 (d, $^2J_{HH}$ = 15.3 Hz), 7.11-7.14 (m, 4H), 7.23-7.33 (m, 10H), 7.39 (dd, J = 7.5, 10.5 Hz, 4H), 7.64 (m, 5H), 8.03 (t, J = 8.4 Hz, 2H). **^{31}P{^{1}H} NMR**. δ 11.4 (d, J_{PP} = 159.7 Hz, 1P), 17.4 (d, J_{PP} = 159.8 Hz, 1P). **^{11}B{^{1}H} NMR**. No signal observed apart from borosilicate in Varian probe. **^{13}C{^{1}H} NMR** (THF-d_8, 125 MHz): δ 13.63 (br), 26.09 (d, J_{PC} = 23.8 Hz, $Ph_2PCH_2CH_2BR_2$), 26.74, 27.16, 32.32, 32.87, 34.76, 34.85, 98.93, 128.00 (d, J_{PC} = 8.9 Hz, *m*-$Ph_2PCH_2CH_2BR_2$), 128.35 (d, J_{PC} = 9.2 Hz, *m*-$Ph_2PCH_2CH_2BR_2$), 128.44 (d, J_{PC} = 9.2 Hz, *m*-PPh_3), 128.59 (d, J_{PC} = 1.5 Hz, *p*-$Ph_2PCH_2CH_2BR_2$), 129.52 (d, J_{PC} = 1.4 Hz, *p*-PPh_3), 129.86 (d, J_{PC} = 1.3 Hz, *p*-$Ph_2PCH_2CH_2BR_2$), 132.50 (d, J_{PC} = 9.0 Hz, *o*-$Ph_2PCH_2CH_2BR_2$), 135.31 (d, J_{PC} = 10.6 Hz, *o*-PPh_3), 135.35 (d, J_{PC} = 9.8 Hz, *o*-$Ph_2PCH_2CH_2BR_2$), 137.33 (dd, J_{PC} = 38.5, 2.1 Hz, *ipso*-$Ph_2PCH_2CH_2BR_2$), 139.85 (d, J_{PC} = 40.8 Hz, *ipso*-PPh_3), 142.99 (d, J_{PC} = 46.4 Hz *ipso*-$Ph_2PCH_2CH_2BR_2$), 203.58 (dd, J_{PC} = 8.9, 9.6 Hz, Re-*C*O), 210.16 (dd, J_{PC} = 5.9, 7.2 Hz, Re-*C*O), 297.45 (dd, J_{PC} = 10.6, 12.0, Re*C*(O)CH_2OBR_3). **IR** (THF): υ_{CO}, 1934, 1841; υ_{acyl} 1572 cm^{-1}. **Anal. Calcd. for $C_{44}H_{45}BNaO_4P_2Re$**: C, 57.46; H, 4.93. Found: C, 57.56; H, 4.95.

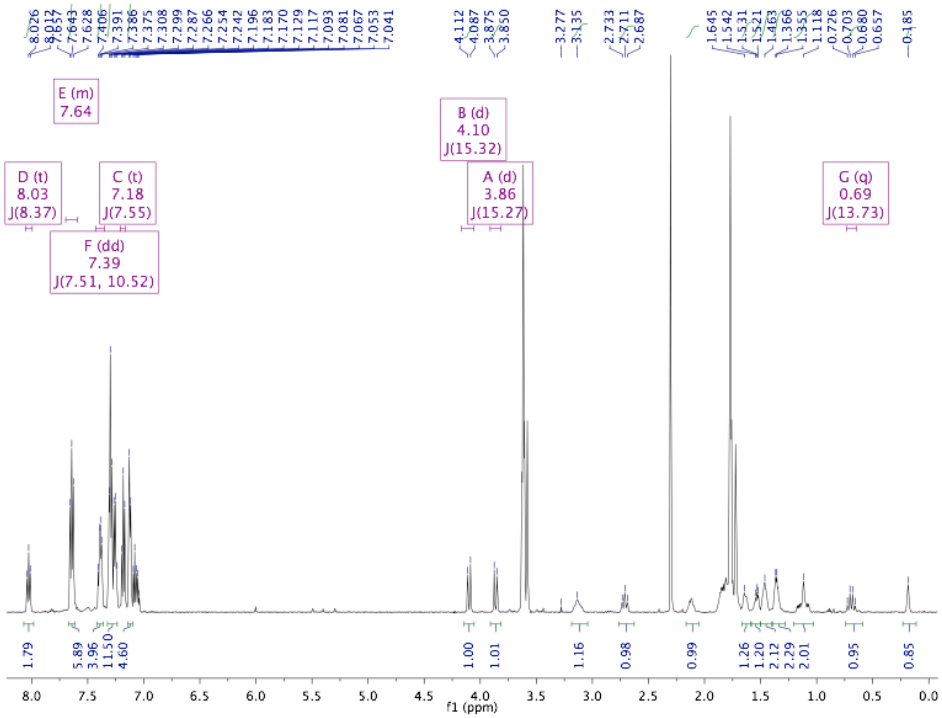


Figure S159. ^{1}H NMR (with some residual toluene).

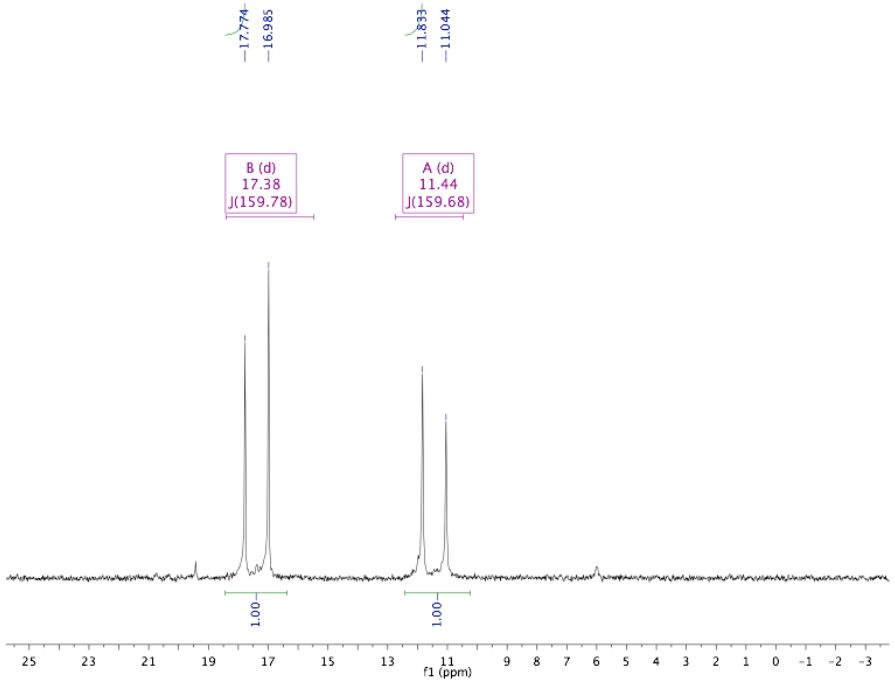


Figure S160. $^{31}P\{^{1}H\}$ NMR.

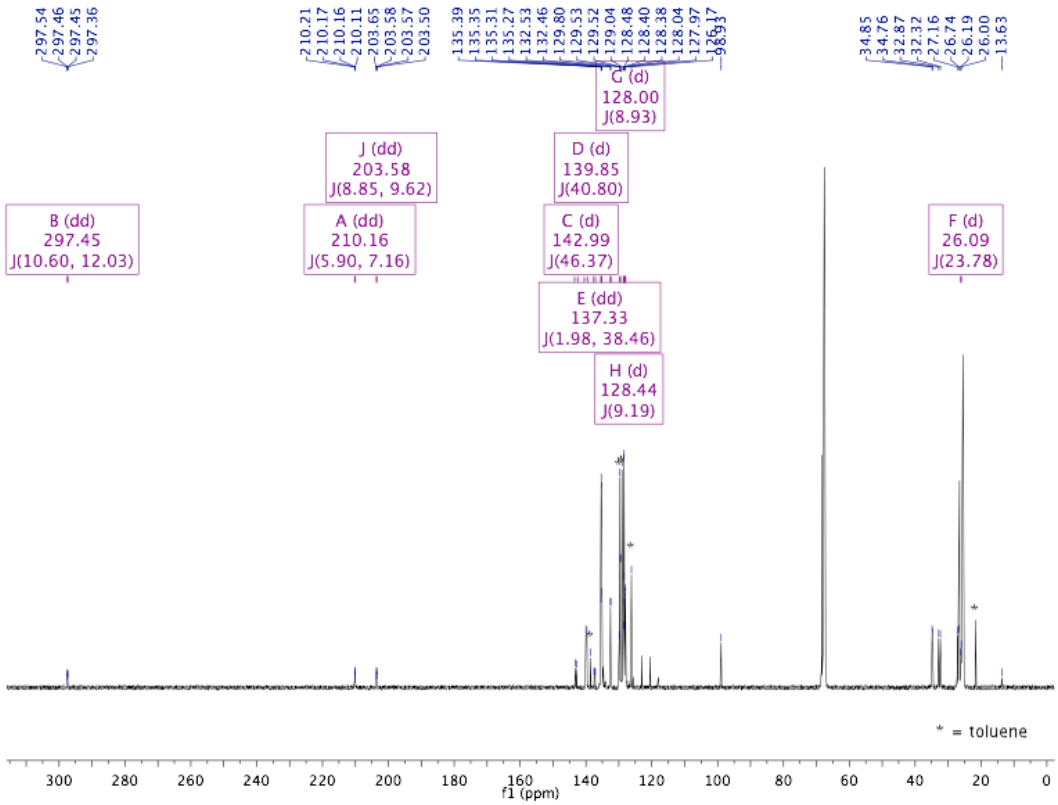


Figure S161. $^{13}C\{^{1}H\}$ NMR.

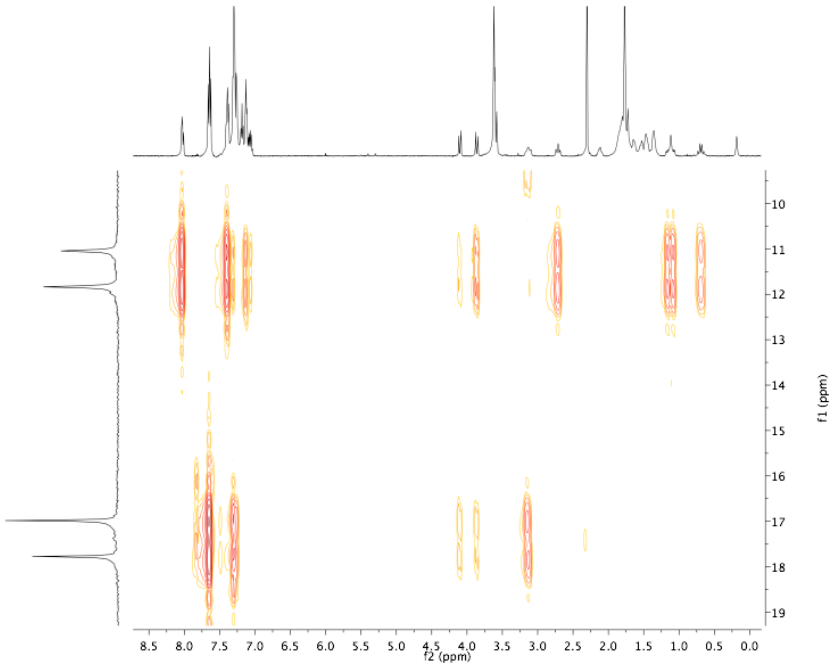


Figure S162. ^{1}H-^{31}P gHMBC.

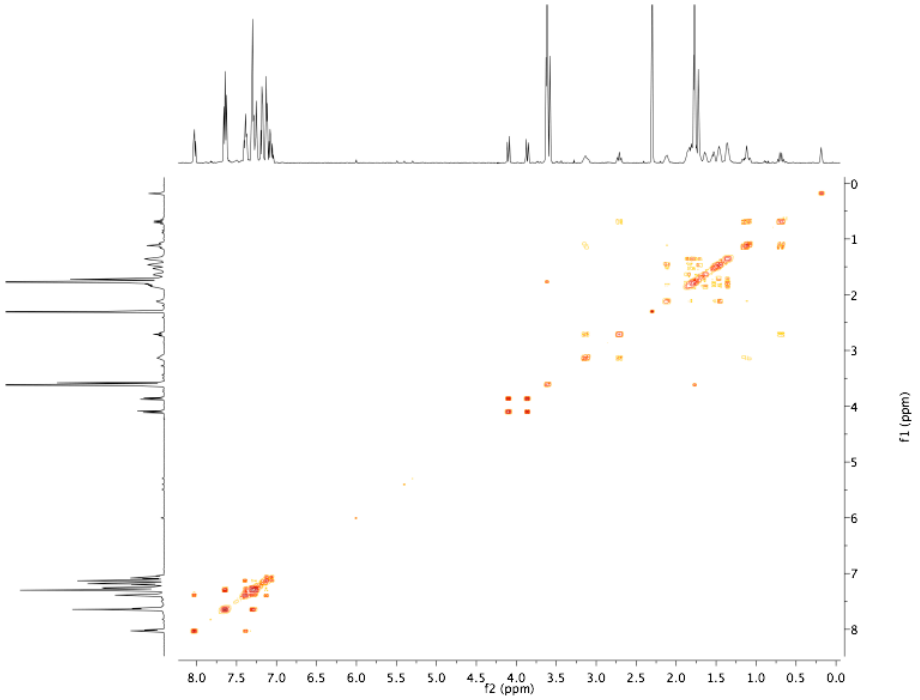


Figure S163. ^{1}H-^{1}H gCOSY.

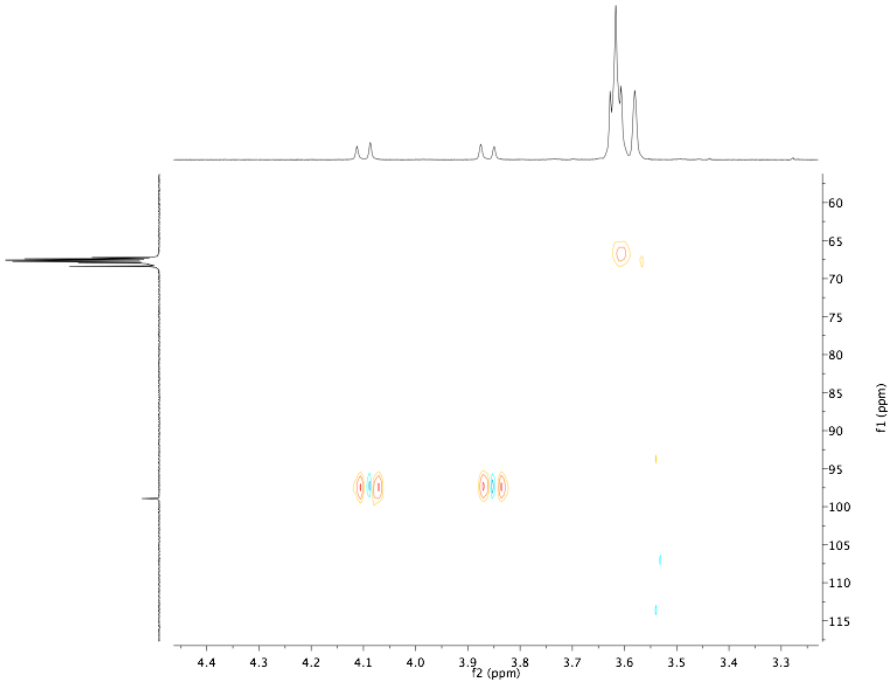


Figure S164. ^{1}H-^{13}C gHMQC NMR showing correlation between Re-C(O)CH_2O- and Re-C(O)CH_2O-.

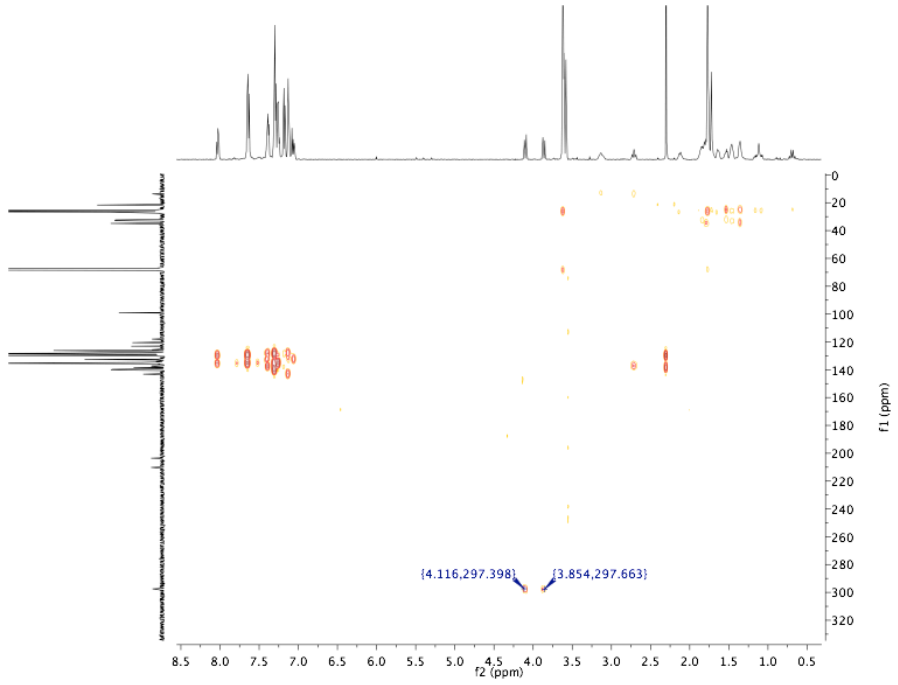


Figure S165. ^{1}H-^{13}C gHMBC, with 2-bond correlation to acyl carbon highlighted.

Reaction of *trans*-[(PPh_3)($Ph_2P(CH_2)_2B(C_8H_{14})$)Re(CO)$_4$][OTf] ([1-$E_1Ph_1$][OTf]) with 2 equiv [HPt][PF_6] (with and without triethylborane).

A vial was charged with 31.9 mg (0.0306 mmol) [**1-E_1Ph_1**][OTf] and ~0.6 mL THF-d_8. With stirring, solid [**HPt**][PF_6] (39.2 mg, 0.0611, 2 equiv) was added, and the mixture was transferred to a J-Young NMR tube. Before monitoring by NMR could begin, most of the Re-containing material had precipitated as boroxycarbene (see above). No further reduction or C-C bond formation products were observed by NMR or when the precipitates were extracted with pyridine.

Separate experiments were carried out under similar conditions, only with 1 and 10 equiv BEt_3 (1.0 M in hexanes) added after the hydride had been added to the Re. Precipitation still occurred, although in the case of 1 equiv, trace C-C coupled products were observed after ~4 hours.

Reaction of [Na][(PPh_3)($Ph_2P(CH_2)_2B(C_8H_{14})$)$Re(CO)_2$(C(O)$CH_2O$—)] with MeOTf.

A 20 mL scintillation vial was charged with 55.3 mg (0.0485 mmol) [$Na(THF)_3$][**3-$E_1$$Ph_1$**] and 2 mL C_6H_5Cl. With stirring, 5.5 μL (0.0485 mmol) MeOTf was added by syringe. The reaction was stirred overnight (NMR studies show reaction to be complete in as little as 30 minutes, however), at which time it was filtered, washed with C_6H_6, and the solvent removed from the filtrate under vacuum, affording 33 mg (0.0362 mmol, 75%) **13** as a yellow powder. Single crystals (large yellow blocks) were grown from vapor diffusion of pentane into a C_6H_5Cl (or C_6H_6) solution of **12**. **^{1}H NMR** (C_6D_6, 500 MHz): δ 1.00 (br, 1H, $Ph_2PCH_2CH_2B(C_8H_{14})$), 1.24 (m, 1H $Ph_2PCH_2CH_2B(C_8H_{14})$), 1.31 (br, 1H, $Ph_2PCH_2CH_2B(C_8H_{14})$), 1.66-1.77 (m, 1H, $Ph_2PCH_2CH_2B(C_8H_{14})$), 1.96-2.47 (m, 12H, $Ph_2PCH_2CH_2B(C_8H_{14})$), 2.74 (m, 1H, $Ph_2PCH_2CH_2B(C_8H_{14})$), 2.80 (3H, Re=C(OC$H_3$)$CH_2O$-), 3.30 (m, 1H, $Ph_2PCH_2CH_2B(C_8H_{14})$), 6.8-6.9 (m, 2H, $Ph_2PCH_2CH_2B(C_8H_{14})$), 6.99 (m, 4H, $Ph_2PCH_2CH_2B(C_8H_{14})$), 7.08 (m, 9H, P$Ph_3$), 7.65 (m, 2H, $Ph_2PCH_2CH_2B(C_8H_{14})$), 7.71 (m, 6H, P$Ph_3$), 7.84 (m, 2H, $Ph_2PCH_2CH_2B(C_8H_{14})$). **^{31}P{^{1}H} NMR** (C_6D_6, 202 MHz): δ 5.7 (d, $^2J_{PP}$ = 114.2 Hz, 1P), 13.5 (d, $^2J_{PP}$ = 114.3 Hz, 1P). **^{13}C{^{1}H} NMR** (C_6D_6, 126 MHz): δ 15.00 (br), 24.39 (br), 24.90 (br), 26.06 ($Ph_2PCH_2CH_2B(C_8H_{14})$), 26.51 ($Ph_2PCH_2CH_2B(C_8H_{14})$), 27.96 (d, J_{PC} = 26.1 Hz, $Ph_2PCH_2CH_2B(C_8H_{14})$), 32.00 ($Ph_2PCH_2CH_2B(C_8H_{14})$), 32.25 ($Ph_2PCH_2CH_2B(C_8H_{14})$), 34.05 ($Ph_2PCH_2CH_2B(C_8H_{14})$), 34.51 ($Ph_2PCH_2CH_2B(C_8H_{14})$), 66.55 (Re=C(O$CH_3$)$CH_2O$-), 90.99 (Re=C($OCH_3$)$CH_2O$-), 128.55 (d, JPC = 9.1 Hz, *m*-$Ph_2PCH_2CH_2B(C_8H_{14})$), 128.74 (d, J_{PC} = 9.7 Hz, *m*-PPh_3), 130.36 (*p*-PPh_3), 130.79 (d, J_{PC} = 8.7 Hz, *p*-$Ph_2PCH_2CH_2B(C_8H_{14})$), 133.72 (d, J_{PC} = 9.2 Hz, *o*-$Ph_2PCH_2CH_2B(C_8H_{14})$), 133.86 (d, J_{PC} = 10.7 Hz, *o*-PPh_3), 136.73 (d, J_{PC} = 45.2 Hz, *ipso*-PPh_3), 144.75 (d, J_{PC} = 46.6 Hz, *ipso*-$Ph_2PCH_2CH_2B(C_8H_{14})$), 203.43 (br t, J_{PC} ~ 7.9 Hz,

*C*O), 209.03 (br t, J_{PC} ~ 9.9 Hz, *C*O), 307.18 (br, Re=*C*(OCH$_3$)CH$_2$O-). **IR** (C$_6$H$_6$): υ_{CO}, 1989, 1857 cm^{-1}. Anal. calcd. for $C_{45}H_{48}BO_4P_2Re$: C, 59.27; H, 5.31. Found: C, 59.54; H, 5.26; N, <0.02.

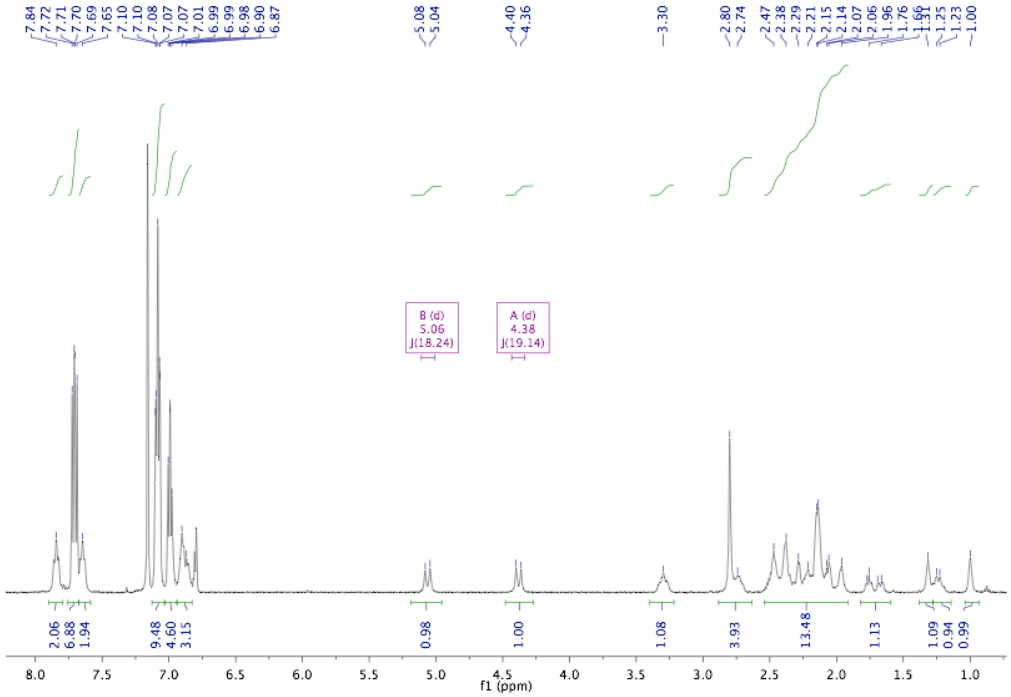


Figure S166. ^{1}H NMR.

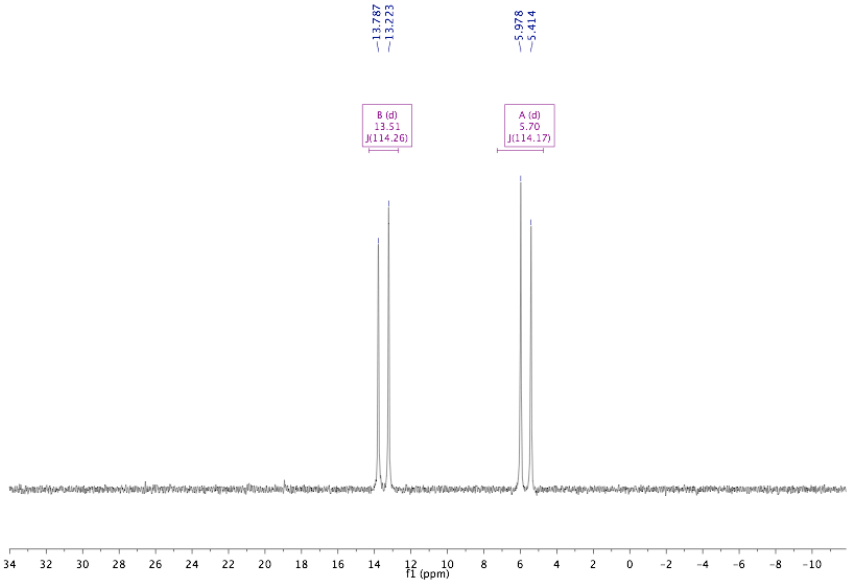


Figure S167. ^{31}P{^{1}H} NMR.

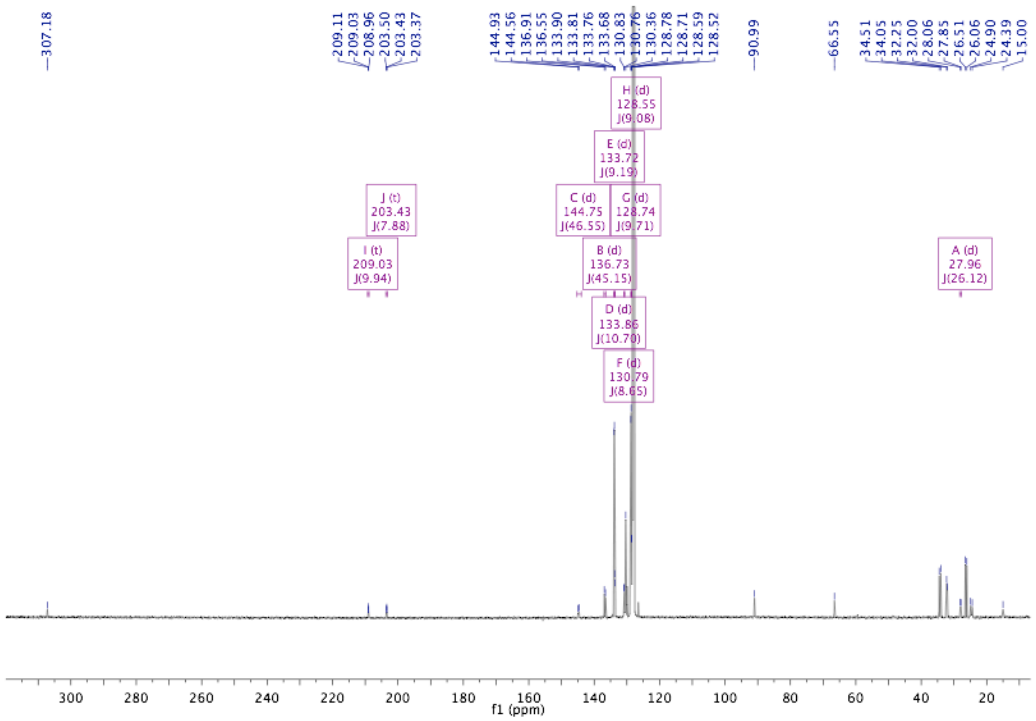


Figure S168. $^{13}C\{^{1}H\}$ NMR.

E. Reductions of [($Ph_2P(CH_2)_3B(C_8H_{14})$)$Re(CO)_5$][OTf] ([1-$P_1$][OTf]).

Reaction of [1-P_1][OTf] with [HPt][PF_6].

A 10 mL scintillation vial was charged with 24.6 mg (0.0299 mmol) [**1-P_1**][OTf], which was dissolved in ~0.6 mL C_6D_5Cl. To the stirring solution was added 19.2 mg (0.0299 mmol) [**HPt**]$^+$ as a solid portionwise. After stirring for a couple minutes, the mixture was transferred to a J-Young NMR tube, and monitored by ^{1}H and $^{31}P\{^{1}H\}$ NMR. After 30 minutes, the ratio of formyl: Re-H was 1.00:0.03. After 1.5 hours, the ratio was 1.00:0.61. After 2.5 hours the ratio was 1.00:28.68. After 5.5 hours, all of the formyl was consumed. During the course of the reaction what appeared to be a Re-alkyl (4.72, d, J_{PH} = 6.6 Hz) was present; the small (~10 %) amount remained constant over the course of the reaction. NMR spectra data for Re-CHO species: **^{1}H NMR** (C_6D_5Cl, 300 MHz): δ 0.89 (br, 2H, $Ph_2PCH_2CH_2CH_2B(C_8H_{14})$), 1.04 (br, 2H,

$Ph_2PCH_2CH_2CH_2B(C_8H_{14})$), 1.52-1.86 (m, 12H, $Ph_2PCH_2CH_2CH_2B(C_8H_{14})$), 1.98 (m, 2H, $Ph_2PCH_2CH_2CH_2B(C_8H_{14})$), 2.51 (m, 2H, $Ph_2PCH_2CH_2CH_2B(C_8H_{14})$), 7.19 (m, 6H, $Ph_2PCH_2CH_2CH_2B(C_8H_{14})$), 7.42-7.49 (m, 4H, $Ph_2PCH_2CH_2CH_2B(C_8H_{14})$), 13.71 (1H, Re-C*H*O). **$^{31}P\{^1H\}$ NMR** (C_6D_5Cl, 121 MHz): δ 1.7.

In a separate reaction, 5.2 mg (0.0063 mmol) [**3C**-**1**][OTf] was dissolved in 0.5 mL CH_2Cl_2 and treated with 4.1 mg (0.0063 mmol) [**HPt**][PF_6]. The reaction mixture was transferred to a solution IR cell for analysis, which showed nearly complete reaction to a formyl species (small amounts of residual starting material were observed). **IR** (CH_2Cl_2): ν_{CO} 2100 (m), 2018 (m), 1983 (s), 1939 (sh), ν_{CHO} 1508 cm^{-1}.

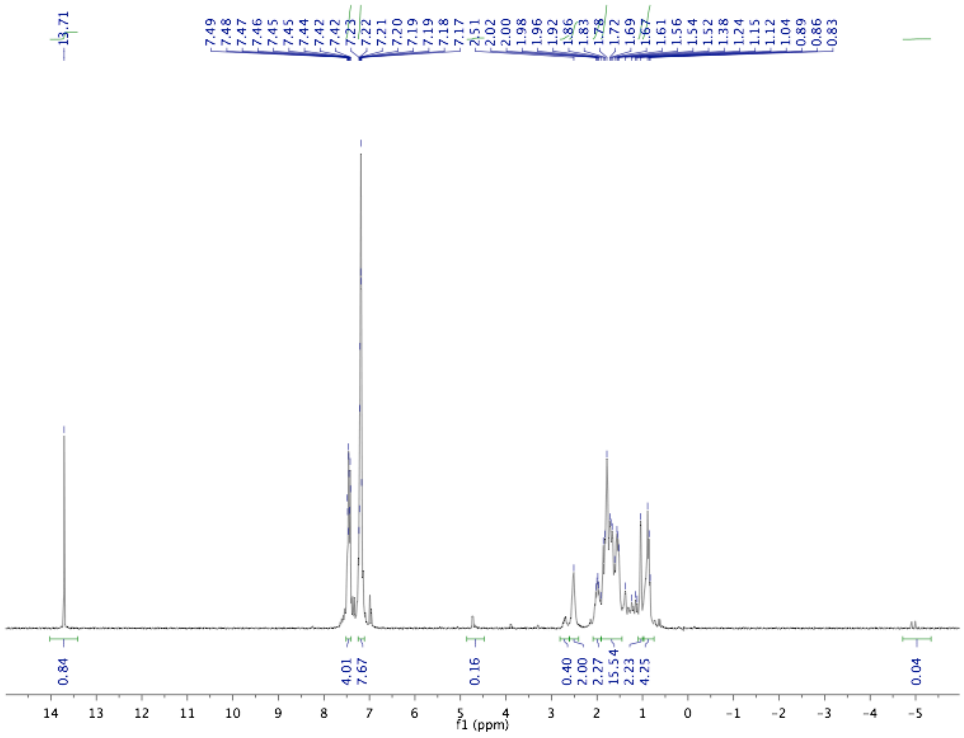


Figure S169. ^1H NMR (initial, mostly Re-CHO).

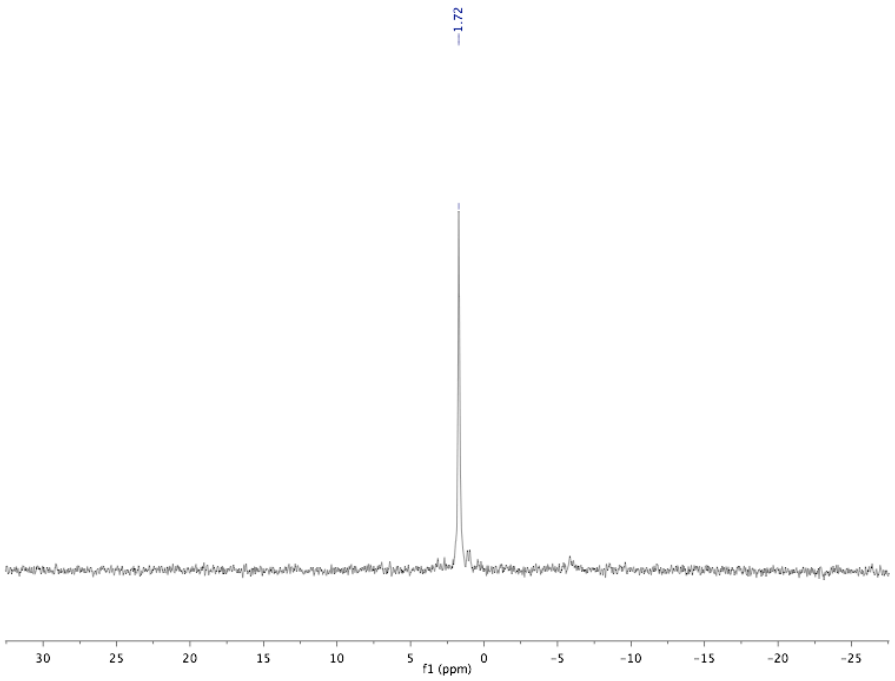


Figure S170. $^{31}P\{^{1}H\}$ NMR (initial, mostly Re-CHO).

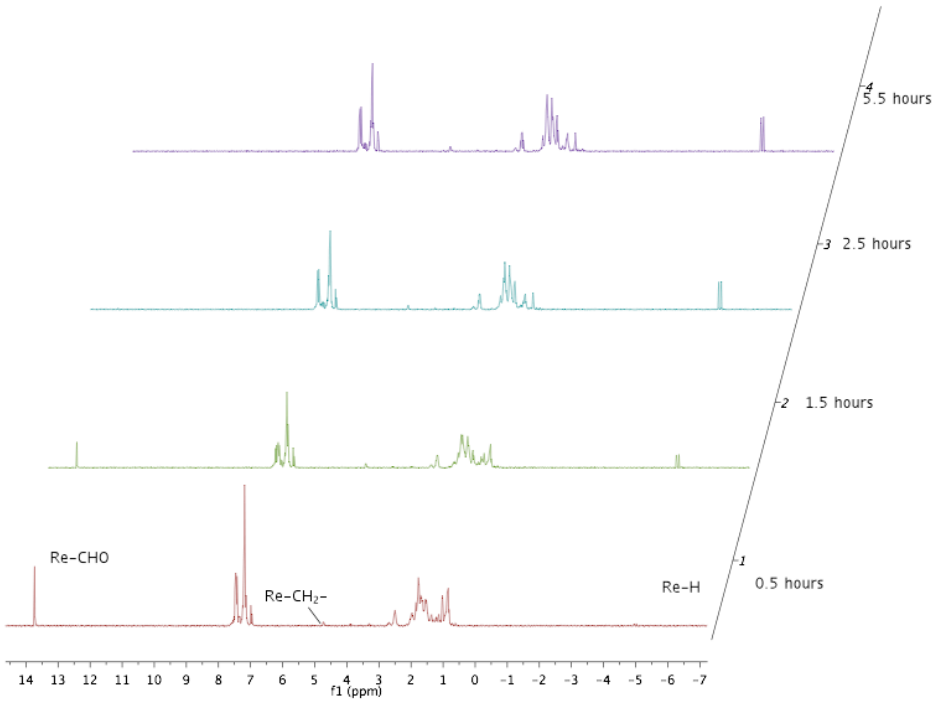


Figure S171. ^{1}H NMR time course.

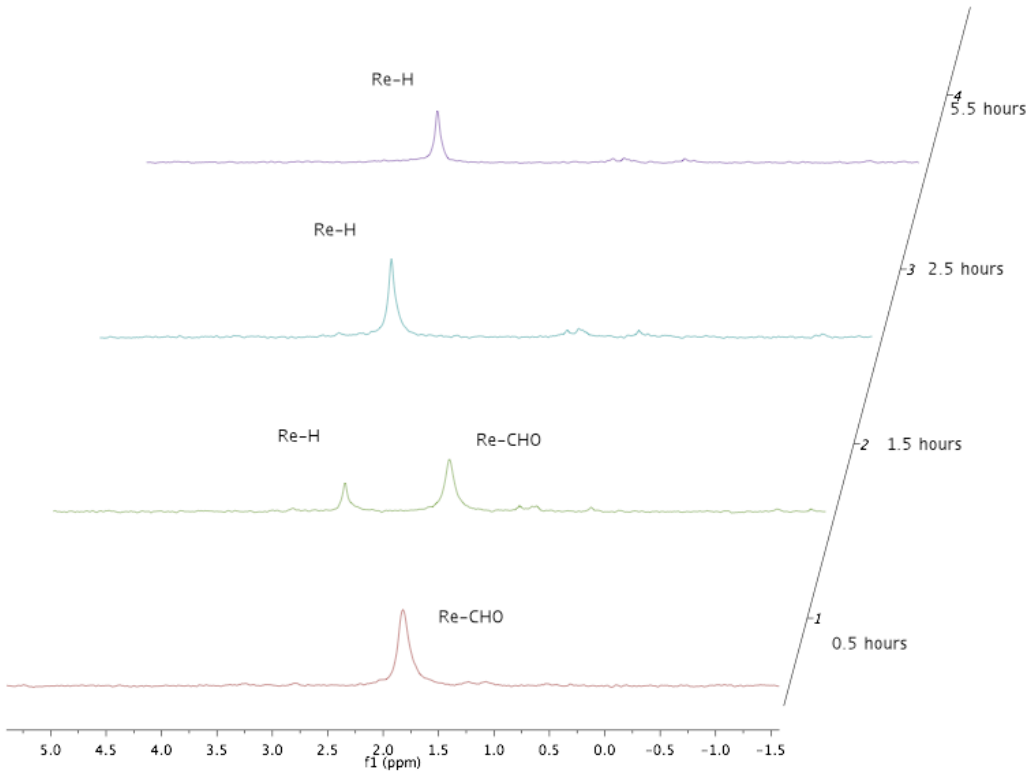


Figure S172. $^{31}P\{^{1}H\}$ NMR time course.

VII. Crystallographic Details.

Table 1. Crystal data and structure refinement for 2-Ph_2•BEt_3 (AJMM59) (CCDC 770577).

Empirical formula	$C_{46}H_{46}BO_4P_2Re \bullet C_7H_8$	
Formula weight	1013.91	
Crystallization Solvent	Toluene	
Crystal Habit	Fragment	
Crystal size	0.19 x 0.19 x 0.06 mm^3	
Crystal color	Colorless	

Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 9878 reflections used in lattice determination	2.46 to 28.81°	
Unit cell dimensions	a = 14.9591(6) Å	
	b = 25.5104(9) Å	β= 105.268(2)°
	c = 25.5702(10) Å	
Volume	9413.5(6) $Å^3$	
Z	8	
Crystal system	Monoclinic	
Space group	P $2_1/n$	
Density (calculated)	1.431 Mg/m^3	
F(000)	4112	
Data collection program	Bruker APEX2 v2009.7-0	

θ range for data collection	1.43 to 28.89°
Completeness to θ = 28.89°	99.7 %
Index ranges	$-20 \leq h \leq 19$, $-34 \leq k \leq 34$, $-34 \leq l \leq 34$
Data collection scan type	ω scans; 11 settings
Data reduction program	Bruker SAINT-Plus v7.66A
Reflections collected	204531
Independent reflections	24722 [R_{int}= 0.0570]
Absorption coefficient	2.694 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7458 and 0.6015

Table 1 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	24722 / 0 / 1107
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.689
Final R indices [I>2σ(I), 19590 reflections]	R1 = 0.0325, *w*R2 = 0.0499
R indices (all data)	R1 = 0.0491, *w*R2 = 0.0515
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.005
Average shift/error	0.000
Largest diff. peak and hole	2.003 and -1.706 e.Å^{-3}

Special Refinement Details

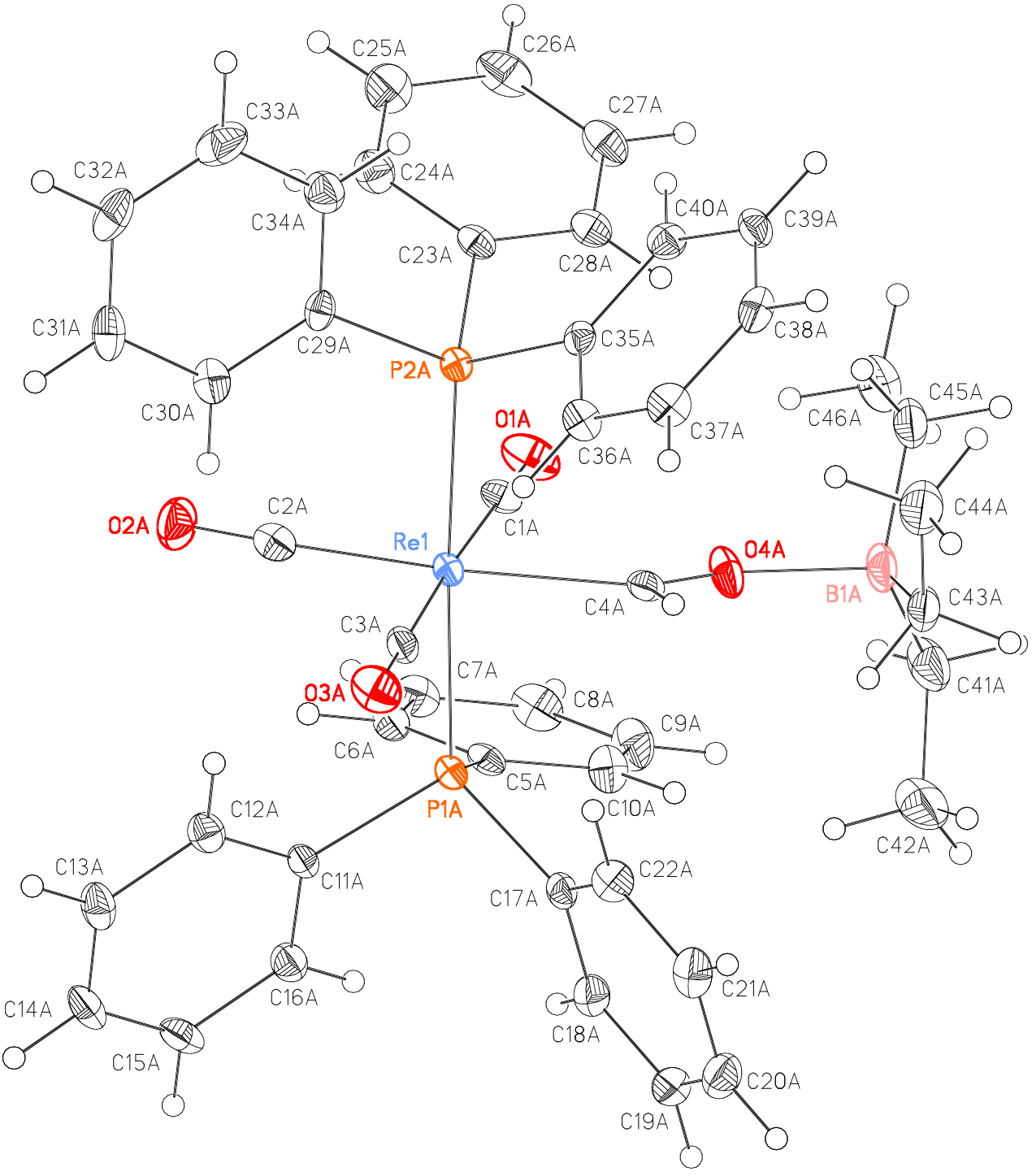
Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

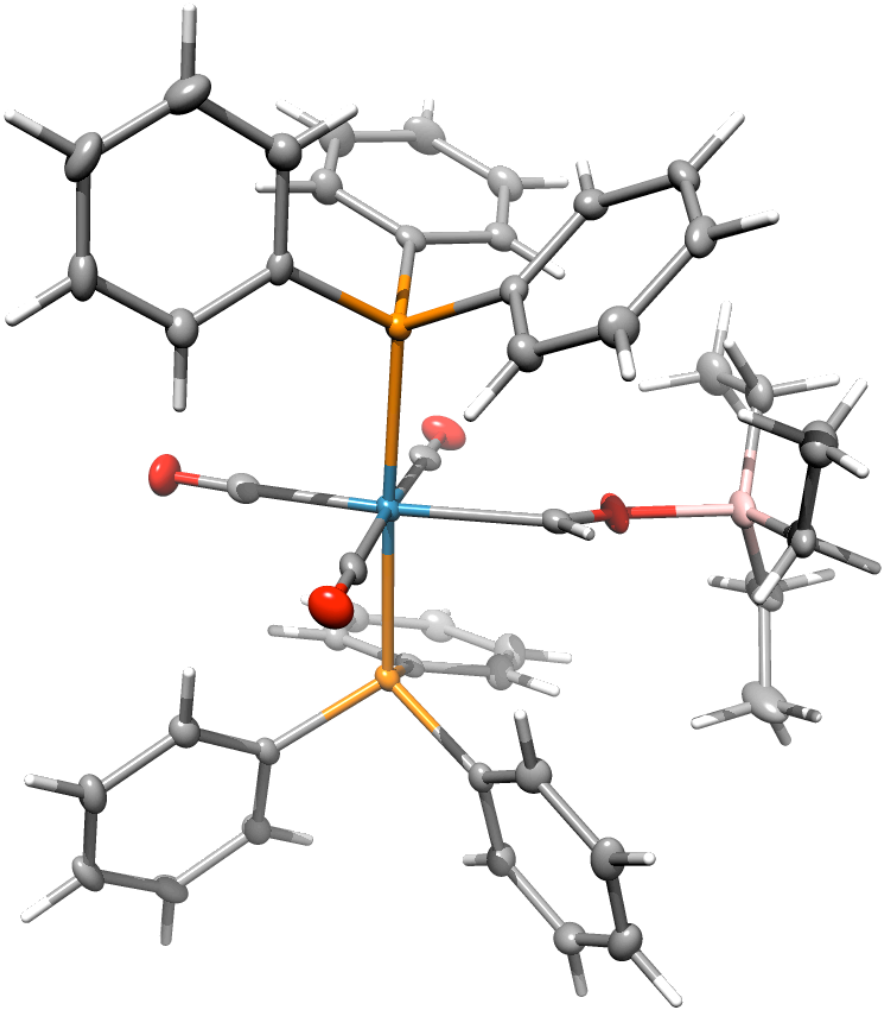
The crystal contains two molecules per asymmetric unit with each molecule accompanied by a toluene solvent of crystallization.

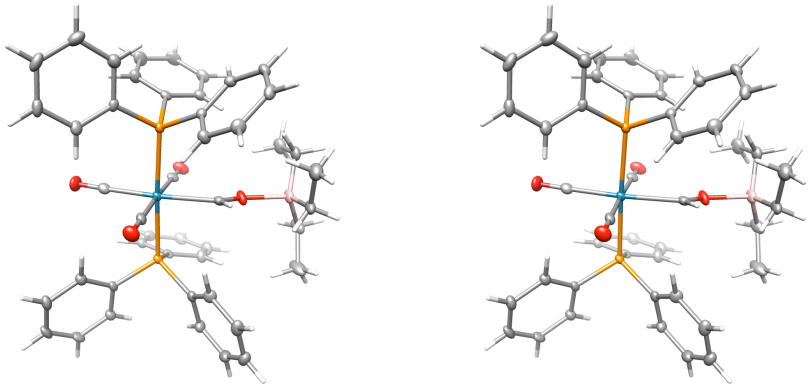
Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will

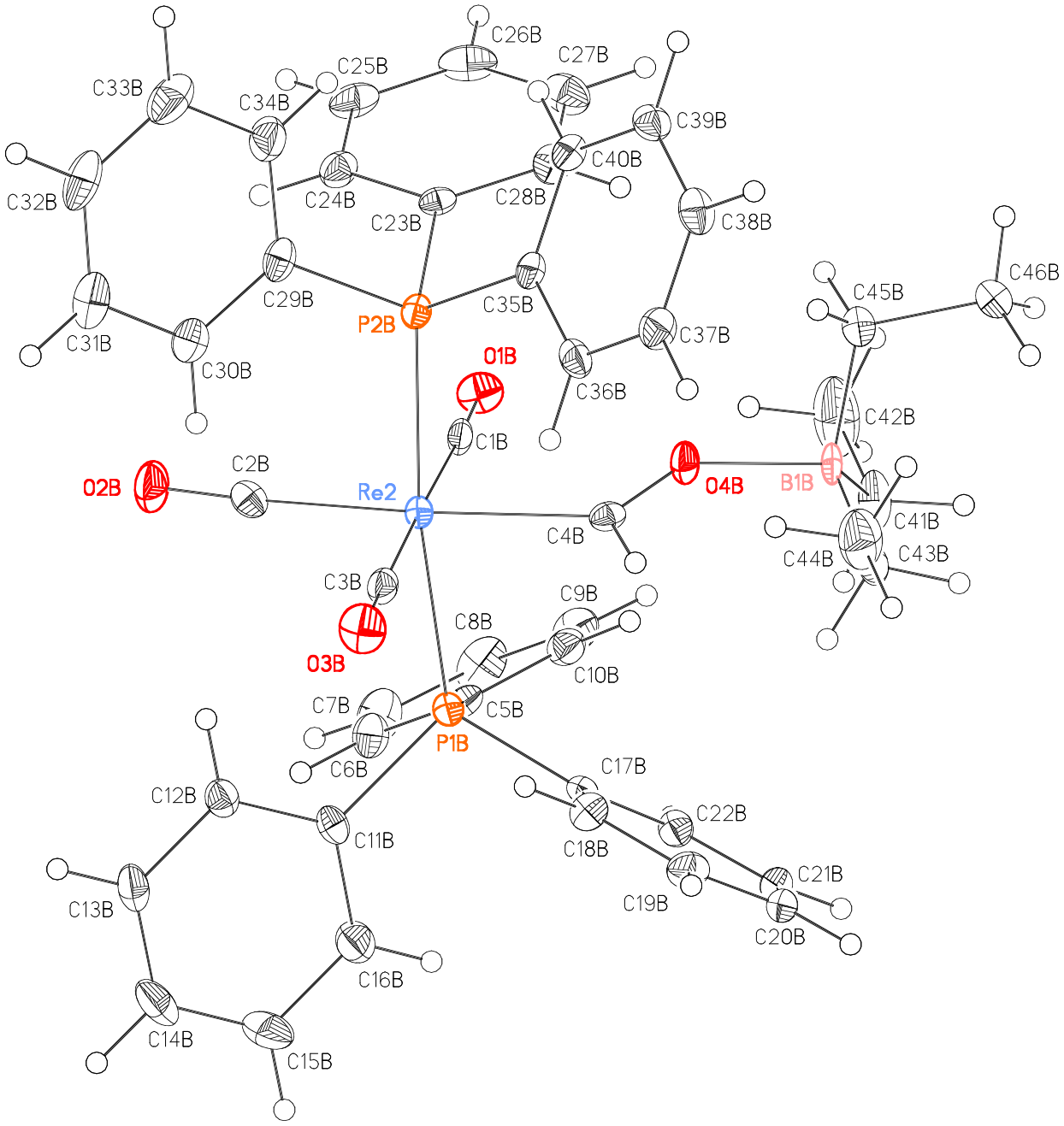
be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.


C25A
C26A
C27A
C33A
C32A
C24A
C34A
C40A
C39A
C23A
C28A
C31A
C29A
C35A
C38A
P2A
C30A
O1A
C36A
C37A
C45A
C46A
O2A
C2A
C1A
C44A
Re1
O4A
B1A
C4A
C43A
C3A
C7A
O3A
C8A
C9A
C41A
C6A
C5A
P1A
C10A
C12A
C42A
C13A
C11A
C22A
C17A
C21A
C14A
C16A
C18A
C15A
C20A
C19A






C26B
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C25B
C33B
C34B
C39B
C40B
C32B
C24B
C28B
C23B
C38B
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C45B
C29B
C35B
P2B
C31B
C37B
C30B
01B
C36B
C42B
C1B
C2B
02B
Re2
04B
B1B
C41B
C4B
C44B
C43B
C3B
C9B
C8B
03B
C10B
C7B
C5B
P1B
C17B
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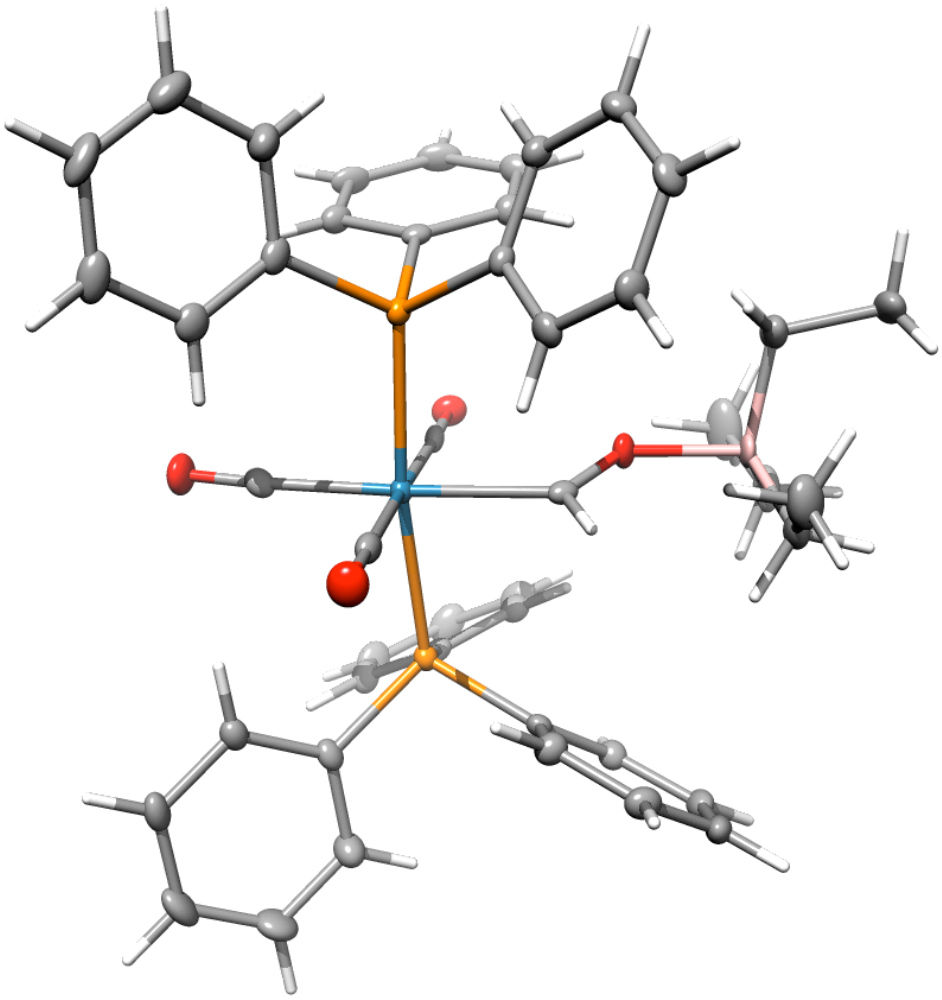
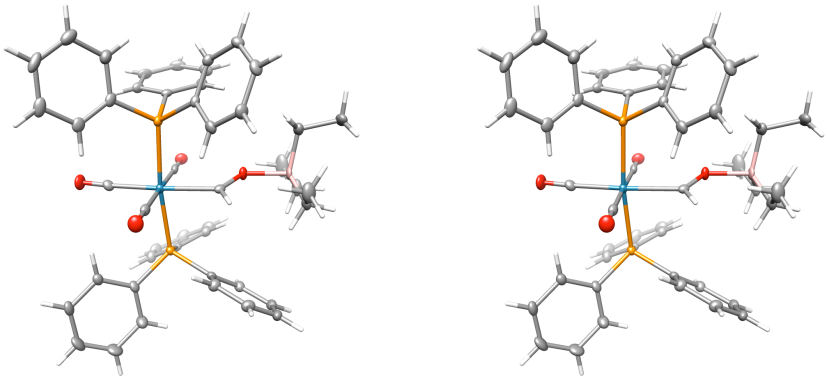
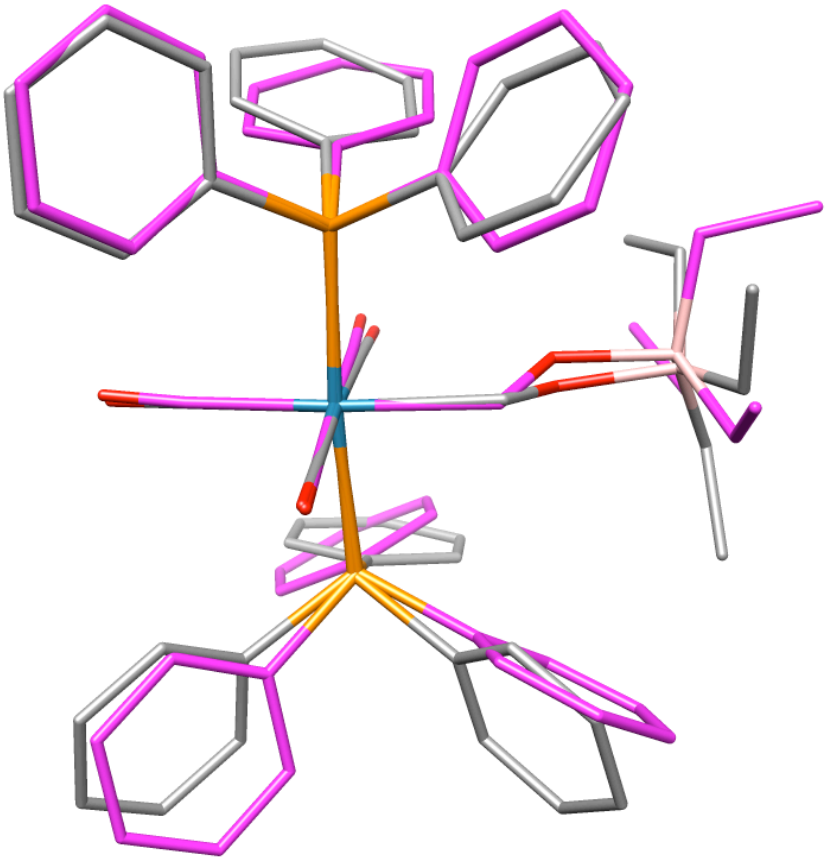
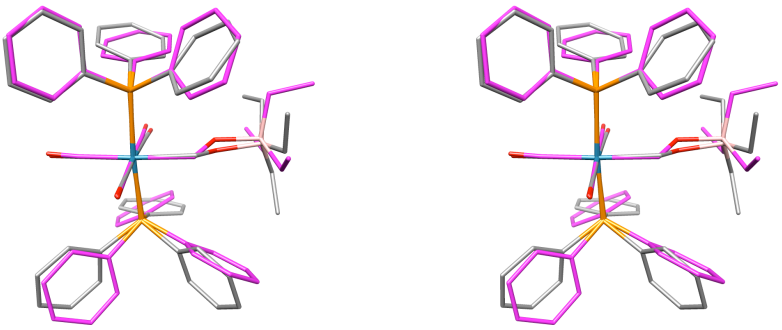
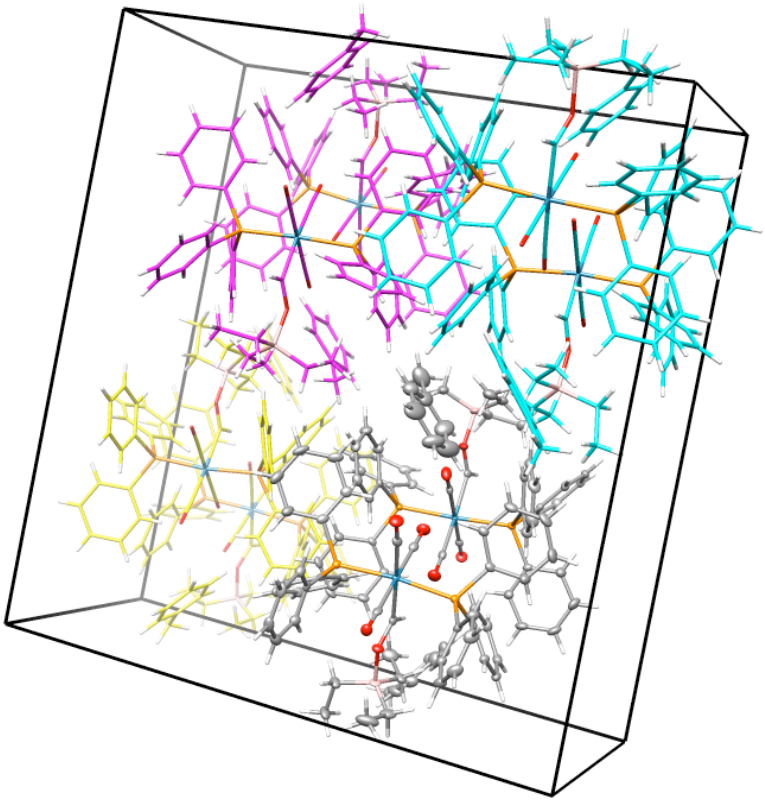
C16B
C14B
C15B











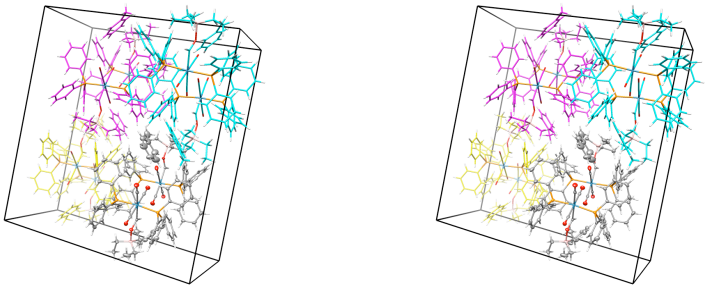


Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 2-Ph_2•BEt_3 (AJMM59) (CCDC 770577). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Re(1)	7124(1)	3019(1)	6560(1)	11(1)
P(1A)	6635(1)	3000(1)	5580(1)	12(1)
P(2A)	7612(1)	3088(1)	7539(1)	12(1)
O(1A)	5428(1)	3758(1)	6516(1)	27(1)
O(2A)	5743(1)	2118(1)	6612(1)	27(1)
O(3A)	8837(1)	2319(1)	6568(1)	25(1)
O(4A)	7461(1)	4169(1)	6408(1)	22(1)
B(1A)	7928(2)	4762(1)	6421(1)	24(1)
C(1A)	6040(2)	3494(1)	6536(1)	17(1)
C(2A)	6289(2)	2433(1)	6597(1)	17(1)
C(3A)	8206(2)	2577(1)	6566(1)	16(1)
C(4A)	7863(2)	3735(1)	6522(1)	16(1)
C(5A)	5554(2)	3360(1)	5322(1)	14(1)
C(6A)	4727(2)	3120(1)	5339(1)	17(1)
C(7A)	3900(2)	3399(1)	5209(1)	22(1)
C(8A)	3892(2)	3918(1)	5060(1)	24(1)
C(9A)	4711(2)	4163(1)	5041(1)	26(1)
C(10A)	5543(2)	3887(1)	5177(1)	21(1)
C(11A)	6350(2)	2354(1)	5256(1)	13(1)
C(12A)	6665(2)	1891(1)	5538(1)	18(1)
C(13A)	6488(2)	1409(1)	5274(1)	21(1)
C(14A)	6011(2)	1387(1)	4735(1)	21(1)
C(15A)	5689(2)	1842(1)	4454(1)	21(1)
C(16A)	5849(2)	2324(1)	4713(1)	18(1)

C(17A)	7415(2)	3268(1)	5199(1)	15(1)
C(18A)	7090(2)	3396(1)	4652(1)	20(1)
C(19A)	7684(2)	3579(1)	4362(1)	23(1)
C(20A)	8621(2)	3634(1)	4611(1)	24(1)
C(21A)	8958(2)	3507(1)	5155(1)	22(1)
C(22A)	8357(2)	3324(1)	5446(1)	19(1)
C(23A)	6733(2)	3411(1)	7803(1)	14(1)
C(24A)	6128(2)	3119(1)	8023(1)	21(1)
C(25A)	5396(2)	3365(1)	8166(1)	27(1)
C(26A)	5272(2)	3900(1)	8100(1)	27(1)
C(27A)	5860(2)	4192(1)	7879(1)	23(1)
C(28A)	6581(2)	3948(1)	7725(1)	18(1)
C(29A)	7845(2)	2483(1)	7938(1)	14(1)
C(30A)	7750(2)	1987(1)	7706(1)	19(1)
C(31A)	7897(2)	1539(1)	8031(1)	23(1)
C(32A)	8146(2)	1584(1)	8587(1)	26(1)
C(33A)	8261(2)	2079(1)	8824(1)	28(1)
C(34A)	8118(2)	2522(1)	8500(1)	21(1)
C(35A)	8698(2)	3442(1)	7831(1)	13(1)
C(36A)	9491(2)	3258(1)	7696(1)	19(1)
C(37A)	10345(2)	3490(1)	7911(1)	20(1)
C(38A)	10427(2)	3911(1)	8259(1)	19(1)
C(39A)	9655(2)	4098(1)	8399(1)	18(1)
C(40A)	8795(2)	3862(1)	8191(1)	17(1)
C(41A)	7402(2)	5005(1)	5840(1)	32(1)
C(42A)	7752(2)	4829(1)	5355(1)	40(1)
C(43A)	9032(2)	4718(1)	6505(1)	26(1)
C(44A)	9641(2)	4657(1)	7089(1)	32(1)
C(45A)	7626(2)	5029(1)	6922(1)	25(1)

C(46A)	6579(2)	5109(1)	6839(1)	35(1)
Re(2)	2064(1)	2200(1)	6557(1)	11(1)
P(1B)	2583(1)	2086(1)	7530(1)	13(1)
P(2B)	1582(1)	2198(1)	5576(1)	13(1)
O(1B)	353(1)	1475(1)	6524(1)	21(1)
O(2B)	699(1)	3115(1)	6601(1)	27(1)
O(3B)	3781(1)	2906(1)	6575(1)	26(1)
O(4B)	2468(1)	1055(1)	6413(1)	17(1)
B(1B)	2982(2)	491(1)	6395(1)	19(1)
C(1B)	983(2)	1729(1)	6539(1)	16(1)
C(2B)	1235(2)	2791(1)	6591(1)	16(1)
C(3B)	3151(2)	2649(1)	6569(1)	16(1)
C(4B)	2818(2)	1501(1)	6518(1)	14(1)
C(5B)	1712(2)	1755(1)	7800(1)	15(1)
C(6B)	1178(2)	2033(1)	8079(1)	20(1)
C(7B)	450(2)	1789(1)	8224(1)	28(1)
C(8B)	255(2)	1266(1)	8102(1)	29(1)
C(9B)	785(2)	985(1)	7826(1)	25(1)
C(10B)	1497(2)	1231(1)	7669(1)	19(1)
C(11B)	2885(2)	2662(1)	7965(1)	16(1)
C(12B)	2711(2)	3168(1)	7758(1)	17(1)
C(13B)	2912(2)	3601(1)	8107(1)	22(1)
C(14B)	3294(2)	3526(1)	8654(1)	28(1)
C(15B)	3486(2)	3024(1)	8860(1)	31(1)
C(16B)	3283(2)	2596(1)	8518(1)	24(1)
C(17B)	3649(2)	1694(1)	7764(1)	14(1)
C(18B)	4433(2)	1880(1)	7627(1)	18(1)
C(19B)	5262(2)	1604(1)	7778(1)	20(1)

C(20B)	5314(2)	1139(1)	8060(1)	20(1)
C(21B)	4536(2)	952(1)	8200(1)	20(1)
C(22B)	3711(2)	1233(1)	8059(1)	16(1)
C(23B)	492(2)	1844(1)	5344(1)	14(1)
C(24B)	-330(2)	2104(1)	5342(1)	18(1)
C(25B)	-1158(2)	1829(1)	5249(1)	22(1)
C(26B)	-1172(2)	1295(1)	5158(1)	25(1)
C(27B)	-357(2)	1033(1)	5159(1)	24(1)
C(28B)	471(2)	1305(1)	5259(1)	19(1)
C(29B)	1349(2)	2829(1)	5221(1)	18(1)
C(30B)	1647(2)	3300(1)	5486(1)	19(1)
C(31B)	1530(2)	3772(1)	5197(1)	25(1)
C(32B)	1123(2)	3771(1)	4645(1)	29(1)
C(33B)	816(2)	3305(1)	4378(1)	31(1)
C(34B)	924(2)	2838(1)	4667(1)	25(1)
C(35B)	2340(2)	1892(1)	5204(1)	14(1)
C(36B)	3297(2)	1898(1)	5424(1)	18(1)
C(37B)	3886(2)	1691(1)	5138(1)	21(1)
C(38B)	3529(2)	1470(1)	4634(1)	20(1)
C(39B)	2576(2)	1465(1)	4408(1)	18(1)
C(40B)	1994(2)	1676(1)	4692(1)	17(1)
C(41B)	2552(2)	133(1)	6793(1)	30(1)
C(42B)	1498(2)	61(1)	6637(2)	48(1)
C(43B)	4092(2)	552(1)	6633(1)	22(1)
C(44B)	4659(2)	798(1)	6281(1)	35(1)
C(45B)	2637(2)	345(1)	5760(1)	26(1)
C(46B)	2988(2)	-192(1)	5623(1)	32(1)
C(51C)	3286(3)	4895(1)	6250(1)	40(1)

C(52C)	3653(3)	4505(2)	6610(2)	57(1)
C(53C)	3078(3)	4230(2)	6838(2)	66(1)
C(54C)	2135(3)	4323(1)	6713(2)	51(1)
C(55C)	1764(3)	4725(2)	6363(2)	63(1)
C(56C)	2353(2)	5017(1)	6116(2)	36(1)
C(57C)	3948(3)	5197(2)	5981(2)	58(1)
C(51D)	8396(2)	91(1)	6036(1)	30(1)
C(52D)	8814(2)	506(1)	6354(1)	34(1)
C(53D)	8349(2)	795(1)	6659(1)	41(1)
C(54D)	7460(2)	671(1)	6657(2)	41(1)
C(55D)	7024(2)	254(1)	6335(2)	47(1)
C(56D)	7494(2)	-28(1)	6033(2)	41(1)
C(57D)	8903(2)	-226(1)	5708(1)	38(1)

Table 3. Selected bond lengths [Å] and angles [°] for 2-Ph_2•BEt_3 (AJMM59) (CCDC 770577).

Re(1)-C(3A)	1.970(3)	C(3A)-Re(1)-C(2A)	95.39(11)
Re(1)-C(2A)	1.967(3)	C(3A)-Re(1)-C(1A)	177.61(11)
Re(1)-C(1A)	2.011(3)	C(2A)-Re(1)-C(1A)	86.68(11)
Re(1)-C(4A)	2.150(3)	C(3A)-Re(1)-C(4A)	93.25(11)
Re(1)-P(1A)	2.4193(7)	C(2A)-Re(1)-C(4A)	171.35(10)
Re(1)-P(2A)	2.4209(7)	C(1A)-Re(1)-C(4A)	84.68(11)
		C(3A)-Re(1)-P(1A)	91.13(8)
		C(2A)-Re(1)-P(1A)	90.61(8)
		C(1A)-Re(1)-P(1A)	87.64(8)
		C(4A)-Re(1)-P(1A)	89.43(7)
		C(3A)-Re(1)-P(2A)	90.62(8)
		C(2A)-Re(1)-P(2A)	91.63(8)
		C(1A)-Re(1)-P(2A)	90.52(8)
		C(4A)-Re(1)-P(2A)	88.06(7)
		P(1A)-Re(1)-P(2A)	177.02(2)

Table 4. Bond lengths [Å] and angles [°] for 2-Ph_2•BEt_3 (AJMM59) (CCDC 770577).

Re(1)-C(3A)	1.970(3)	C(11A)-C(16A)	1.396(4)
Re(1)-C(2A)	1.967(3)	C(12A)-C(13A)	1.396(4)
Re(1)-C(1A)	2.011(3)	C(13A)-C(14A)	1.377(4)
Re(1)-C(4A)	2.150(3)	C(14A)-C(15A)	1.383(4)
Re(1)-P(1A)	2.4193(7)	C(15A)-C(16A)	1.389(4)
Re(1)-P(2A)	2.4209(7)	C(17A)-C(22A)	1.392(3)
P(1A)-C(5A)	1.826(3)	C(17A)-C(18A)	1.393(4)
P(1A)-C(17A)	1.837(3)	C(18A)-C(19A)	1.381(4)
P(1A)-C(11A)	1.841(3)	C(19A)-C(20A)	1.386(4)
P(2A)-C(23A)	1.825(3)	C(20A)-C(21A)	1.387(4)
P(2A)-C(29A)	1.834(3)	C(21A)-C(22A)	1.390(4)
P(2A)-C(35A)	1.838(3)	C(23A)-C(24A)	1.398(4)
O(1A)-C(1A)	1.128(3)	C(23A)-C(28A)	1.394(4)
O(2A)-C(2A)	1.153(3)	C(24A)-C(25A)	1.391(4)
O(3A)-C(3A)	1.149(3)	C(25A)-C(26A)	1.383(4)
O(4A)-C(4A)	1.257(3)	C(26A)-C(27A)	1.380(4)
O(4A)-B(1A)	1.662(4)	C(27A)-C(28A)	1.391(4)
B(1A)-C(41A)	1.609(4)	C(29A)-C(34A)	1.391(4)
B(1A)-C(45A)	1.618(5)	C(29A)-C(30A)	1.389(4)
B(1A)-C(43A)	1.612(4)	C(30A)-C(31A)	1.396(4)
C(5A)-C(6A)	1.393(4)	C(31A)-C(32A)	1.375(4)
C(5A)-C(10A)	1.393(4)	C(32A)-C(33A)	1.390(4)
C(6A)-C(7A)	1.389(4)	C(33A)-C(34A)	1.385(4)
C(7A)-C(8A)	1.376(4)	C(35A)-C(36A)	1.402(4)
C(8A)-C(9A)	1.387(4)	C(35A)-C(40A)	1.395(4)
C(9A)-C(10A)	1.391(4)	C(36A)-C(37A)	1.384(4)
C(11A)-C(12A)	1.399(4)	C(37A)-C(38A)	1.380(4)

C(38A)-C(39A)	1.381(4)	C(8B)-C(9B)	1.392(4)
C(39A)-C(40A)	1.393(3)	C(9B)-C(10B)	1.382(4)
C(41A)-C(42A)	1.537(4)	C(11B)-C(16B)	1.392(4)
C(43A)-C(44A)	1.540(4)	C(11B)-C(12B)	1.394(4)
C(45A)-C(46A)	1.537(4)	C(12B)-C(13B)	1.402(4)
Re(2)-C(2B)	1.969(3)	C(13B)-C(14B)	1.377(4)
Re(2)-C(3B)	1.981(3)	C(14B)-C(15B)	1.386(4)
Re(2)-C(1B)	2.005(3)	C(15B)-C(16B)	1.383(4)
Re(2)-C(4B)	2.126(3)	C(17B)-C(18B)	1.394(3)
Re(2)-P(2B)	2.4193(7)	C(17B)-C(22B)	1.388(4)
Re(2)-P(1B)	2.4216(7)	C(18B)-C(19B)	1.390(4)
P(1B)-C(11B)	1.827(3)	C(19B)-C(20B)	1.380(4)
P(1B)-C(5B)	1.832(3)	C(20B)-C(21B)	1.389(4)
P(1B)-C(17B)	1.843(3)	C(21B)-C(22B)	1.390(3)
P(2B)-C(23B)	1.822(3)	C(23B)-C(24B)	1.396(3)
P(2B)-C(35B)	1.837(3)	C(23B)-C(28B)	1.391(4)
P(2B)-C(29B)	1.836(3)	C(24B)-C(25B)	1.388(4)
O(1B)-C(1B)	1.137(3)	C(25B)-C(26B)	1.381(4)
O(2B)-C(2B)	1.156(3)	C(26B)-C(27B)	1.389(4)
O(3B)-C(3B)	1.146(3)	C(27B)-C(28B)	1.384(4)
O(4B)-C(4B)	1.252(3)	C(29B)-C(30B)	1.394(4)
O(4B)-B(1B)	1.638(3)	C(29B)-C(34B)	1.391(4)
B(1B)-C(45B)	1.612(4)	C(30B)-C(31B)	1.401(4)
B(1B)-C(43B)	1.618(4)	C(31B)-C(32B)	1.382(4)
B(1B)-C(41B)	1.620(4)	C(32B)-C(33B)	1.388(4)
C(5B)-C(6B)	1.396(4)	C(33B)-C(34B)	1.388(4)
C(5B)-C(10B)	1.396(4)	C(35B)-C(36B)	1.393(3)
C(6B)-C(7B)	1.387(4)	C(35B)-C(40B)	1.389(4)
C(7B)-C(8B)	1.382(4)	C(36B)-C(37B)	1.389(4)

C(37B)-C(38B)	1.379(4)	C(1A)-Re(1)-P(1A)	87.64(8)
C(38B)-C(39B)	1.389(4)	C(4A)-Re(1)-P(1A)	89.43(7)
C(39B)-C(40B)	1.380(4)	C(3A)-Re(1)-P(2A)	90.62(8)
C(41B)-C(42B)	1.533(4)	C(2A)-Re(1)-P(2A)	91.63(8)
C(43B)-C(44B)	1.526(4)	C(1A)-Re(1)-P(2A)	90.52(8)
C(45B)-C(46B)	1.540(4)	C(4A)-Re(1)-P(2A)	88.06(7)
C(51C)-C(52C)	1.367(5)	P(1A)-Re(1)-P(2A)	177.02(2)
C(51C)-C(56C)	1.382(4)	C(5A)-P(1A)-C(17A)	104.27(12)
C(51C)-C(57C)	1.551(5)	C(5A)-P(1A)-C(11A)	102.12(12)
C(52C)-C(53C)	1.354(5)	C(17A)-P(1A)-C(11A)	101.46(12)
C(53C)-C(54C)	1.382(5)	C(5A)-P(1A)-Re(1)	111.21(9)
C(54C)-C(55C)	1.379(5)	C(17A)-P(1A)-Re(1)	118.68(9)
C(55C)-C(56C)	1.422(5)	C(11A)-P(1A)-Re(1)	117.08(9)
C(51D)-C(56D)	1.381(4)	C(23A)-P(2A)-C(29A)	102.89(12)
C(51D)-C(52D)	1.383(4)	C(23A)-P(2A)-C(35A)	105.90(12)
C(51D)-C(57D)	1.504(4)	C(29A)-P(2A)-C(35A)	99.72(12)
C(52D)-C(53D)	1.385(5)	C(23A)-P(2A)-Re(1)	111.39(9)
C(53D)-C(54D)	1.365(4)	C(29A)-P(2A)-Re(1)	118.44(9)
C(54D)-C(55D)	1.398(5)	C(35A)-P(2A)-Re(1)	116.75(9)
C(55D)-C(56D)	1.377(5)	C(4A)-O(4A)-B(1A)	128.6(2)
		C(41A)-B(1A)-C(45A)	113.5(3)
C(3A)-Re(1)-C(2A)	95.39(11)	C(41A)-B(1A)-C(43A)	112.6(3)
C(3A)-Re(1)-C(1A)	177.61(11)	C(45A)-B(1A)-C(43A)	114.4(3)
C(2A)-Re(1)-C(1A)	86.68(11)	C(41A)-B(1A)-O(4A)	103.4(2)
C(3A)-Re(1)-C(4A)	93.25(11)	C(45A)-B(1A)-O(4A)	101.3(2)
C(2A)-Re(1)-C(4A)	171.35(10)	C(43A)-B(1A)-O(4A)	110.4(2)
C(1A)-Re(1)-C(4A)	84.68(11)	O(1A)-C(1A)-Re(1)	179.2(3)
C(3A)-Re(1)-P(1A)	91.13(8)	O(2A)-C(2A)-Re(1)	174.5(2)
C(2A)-Re(1)-P(1A)	90.61(8)	O(3A)-C(3A)-Re(1)	179.8(3)

O(4A)-C(4A)-Re(1)	122.6(2)	C(24A)-C(25A)-C(26A)	120.2(3)
C(6A)-C(5A)-C(10A)	119.0(2)	C(27A)-C(26A)-C(25A)	120.2(3)
C(6A)-C(5A)-P(1A)	118.4(2)	C(26A)-C(27A)-C(28A)	119.9(3)
C(10A)-C(5A)-P(1A)	122.0(2)	C(27A)-C(28A)-C(23A)	120.7(3)
C(7A)-C(6A)-C(5A)	120.6(3)	C(34A)-C(29A)-C(30A)	118.5(3)
C(8A)-C(7A)-C(6A)	120.1(3)	C(34A)-C(29A)-P(2A)	118.5(2)
C(7A)-C(8A)-C(9A)	119.9(3)	C(30A)-C(29A)-P(2A)	123.1(2)
C(10A)-C(9A)-C(8A)	120.3(3)	C(31A)-C(30A)-C(29A)	120.6(3)
C(9A)-C(10A)-C(5A)	120.1(3)	C(32A)-C(31A)-C(30A)	120.2(3)
C(12A)-C(11A)-C(16A)	119.0(3)	C(31A)-C(32A)-C(33A)	119.7(3)
C(12A)-C(11A)-P(1A)	121.1(2)	C(32A)-C(33A)-C(34A)	120.0(3)
C(16A)-C(11A)-P(1A)	119.8(2)	C(33A)-C(34A)-C(29A)	121.0(3)
C(13A)-C(12A)-C(11A)	120.1(3)	C(36A)-C(35A)-C(40A)	118.3(2)
C(14A)-C(13A)-C(12A)	120.2(3)	C(36A)-C(35A)-P(2A)	116.7(2)
C(13A)-C(14A)-C(15A)	120.3(3)	C(40A)-C(35A)-P(2A)	125.0(2)
C(14A)-C(15A)-C(16A)	120.2(3)	C(37A)-C(36A)-C(35A)	120.7(3)
C(15A)-C(16A)-C(11A)	120.3(3)	C(36A)-C(37A)-C(38A)	120.4(3)
C(22A)-C(17A)-C(18A)	118.3(2)	C(39A)-C(38A)-C(37A)	119.9(3)
C(22A)-C(17A)-P(1A)	120.5(2)	C(38A)-C(39A)-C(40A)	120.2(3)
C(18A)-C(17A)-P(1A)	121.2(2)	C(39A)-C(40A)-C(35A)	120.5(3)
C(19A)-C(18A)-C(17A)	121.1(3)	C(42A)-C(41A)-B(1A)	116.4(3)
C(18A)-C(19A)-C(20A)	120.2(3)	C(44A)-C(43A)-B(1A)	117.4(3)
C(19A)-C(20A)-C(21A)	119.6(3)	C(46A)-C(45A)-B(1A)	115.5(3)
C(22A)-C(21A)-C(20A)	120.0(3)	C(2B)-Re(2)-C(3B)	94.69(11)
C(21A)-C(22A)-C(17A)	120.9(3)	C(2B)-Re(2)-C(1B)	86.87(11)
C(24A)-C(23A)-C(28A)	118.8(2)	C(3B)-Re(2)-C(1B)	178.41(11)
C(24A)-C(23A)-P(2A)	121.0(2)	C(2B)-Re(2)-C(4B)	172.85(11)
C(28A)-C(23A)-P(2A)	119.8(2)	C(3B)-Re(2)-C(4B)	92.46(10)
C(25A)-C(24A)-C(23A)	120.2(3)	C(1B)-Re(2)-C(4B)	85.99(10)

C(2B)-Re(2)-P(2B)	91.64(8)	O(2B)-C(2B)-Re(2)	175.5(2)
C(3B)-Re(2)-P(2B)	92.13(8)	O(3B)-C(3B)-Re(2)	179.7(3)
C(1B)-Re(2)-P(2B)	87.48(8)	O(4B)-C(4B)-Re(2)	125.18(19)
C(4B)-Re(2)-P(2B)	88.16(7)	C(6B)-C(5B)-C(10B)	118.8(2)
C(2B)-Re(2)-P(1B)	94.66(8)	C(6B)-C(5B)-P(1B)	121.2(2)
C(3B)-Re(2)-P(1B)	90.83(8)	C(10B)-C(5B)-P(1B)	119.5(2)
C(1B)-Re(2)-P(1B)	89.38(8)	C(7B)-C(6B)-C(5B)	120.2(3)
C(4B)-Re(2)-P(1B)	85.16(7)	C(6B)-C(7B)-C(8B)	120.5(3)
P(2B)-Re(2)-P(1B)	172.80(2)	C(7B)-C(8B)-C(9B)	119.7(3)
C(11B)-P(1B)-C(5B)	103.14(13)	C(10B)-C(9B)-C(8B)	120.0(3)
C(11B)-P(1B)-C(17B)	100.56(12)	C(9B)-C(10B)-C(5B)	120.7(3)
C(5B)-P(1B)-C(17B)	105.60(12)	C(16B)-C(11B)-C(12B)	119.0(3)
C(11B)-P(1B)-Re(2)	119.31(9)	C(16B)-C(11B)-P(1B)	119.5(2)
C(5B)-P(1B)-Re(2)	112.06(9)	C(12B)-C(11B)-P(1B)	121.5(2)
C(17B)-P(1B)-Re(2)	114.52(9)	C(11B)-C(12B)-C(13B)	120.1(3)
C(23B)-P(2B)-C(35B)	104.00(12)	C(14B)-C(13B)-C(12B)	119.9(3)
C(23B)-P(2B)-C(29B)	103.70(12)	C(13B)-C(14B)-C(15B)	120.2(3)
C(35B)-P(2B)-C(29B)	100.34(12)	C(16B)-C(15B)-C(14B)	120.1(3)
C(23B)-P(2B)-Re(2)	109.63(9)	C(15B)-C(16B)-C(11B)	120.7(3)
C(35B)-P(2B)-Re(2)	118.77(9)	C(18B)-C(17B)-C(22B)	119.1(2)
C(29B)-P(2B)-Re(2)	118.48(10)	C(18B)-C(17B)-P(1B)	116.6(2)
C(4B)-O(4B)-B(1B)	129.2(2)	C(22B)-C(17B)-P(1B)	124.3(2)
C(45B)-B(1B)-C(43B)	115.2(3)	C(17B)-C(18B)-C(19B)	120.3(3)
C(45B)-B(1B)-C(41B)	115.3(3)	C(20B)-C(19B)-C(18B)	120.3(3)
C(43B)-B(1B)-C(41B)	110.8(2)	C(19B)-C(20B)-C(21B)	119.6(3)
C(45B)-B(1B)-O(4B)	101.7(2)	C(20B)-C(21B)-C(22B)	120.2(3)
C(43B)-B(1B)-O(4B)	110.4(2)	C(21B)-C(22B)-C(17B)	120.4(3)
C(41B)-B(1B)-O(4B)	102.2(2)	C(24B)-C(23B)-C(28B)	119.1(2)
O(1B)-C(1B)-Re(2)	178.0(2)	C(24B)-C(23B)-P(2B)	118.5(2)

C(28B)-C(23B)-P(2B)	121.5(2)	C(52C)-C(53C)-C(54C)	122.5(4)
C(25B)-C(24B)-C(23B)	120.3(3)	C(55C)-C(54C)-C(53C)	119.3(4)
C(26B)-C(25B)-C(24B)	120.1(3)	C(54C)-C(55C)-C(56C)	119.2(4)
C(25B)-C(26B)-C(27B)	119.9(3)	C(51C)-C(56C)-C(55C)	118.3(4)
C(28B)-C(27B)-C(26B)	120.1(3)	C(56D)-C(51D)-C(52D)	117.4(3)
C(27B)-C(28B)-C(23B)	120.4(3)	C(56D)-C(51D)-C(57D)	121.0(3)
C(30B)-C(29B)-C(34B)	118.9(3)	C(52D)-C(51D)-C(57D)	121.6(3)
C(30B)-C(29B)-P(2B)	121.3(2)	C(53D)-C(52D)-C(51D)	121.5(3)
C(34B)-C(29B)-P(2B)	119.6(2)	C(54D)-C(53D)-C(52D)	120.6(3)
C(29B)-C(30B)-C(31B)	120.3(3)	C(53D)-C(54D)-C(55D)	118.7(4)
C(32B)-C(31B)-C(30B)	119.9(3)	C(56D)-C(55D)-C(54D)	120.0(3)
C(31B)-C(32B)-C(33B)	120.2(3)	C(55D)-C(56D)-C(51D)	121.7(3)
C(32B)-C(33B)-C(34B)	119.8(3)		
C(33B)-C(34B)-C(29B)	120.9(3)		
C(36B)-C(35B)-C(40B)	118.3(2)		
C(36B)-C(35B)-P(2B)	119.7(2)		
C(40B)-C(35B)-P(2B)	121.98(19)		
C(37B)-C(36B)-C(35B)	120.7(3)		
C(36B)-C(37B)-C(38B)	120.2(3)		
C(39B)-C(38B)-C(37B)	119.7(3)		
C(40B)-C(39B)-C(38B)	119.9(3)		
C(39B)-C(40B)-C(35B)	121.3(2)		
C(42B)-C(41B)-B(1B)	117.1(3)		
C(44B)-C(43B)-B(1B)	119.5(3)		
C(46B)-C(45B)-B(1B)	113.3(2)		
C(52C)-C(51C)-C(56C)	122.1(4)		
C(52C)-C(51C)-C(57C)	118.0(4)		
C(56C)-C(51C)-C(57C)	119.9(3)		
C(53C)-C(52C)-C(51C)	118.6(4)		

Table 5. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for 2-Ph_2•BEt_3 (AJMM59) (CCDC 770577). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Re(1)	118(1)	98(1)	117(1)	-9(1)	13(1)	4(1)
P(1A)	128(3)	110(4)	128(4)	-15(3)	18(3)	3(3)
P(2A)	123(3)	114(4)	130(4)	-4(3)	25(3)	1(3)
O(1A)	223(11)	313(13)	248(12)	-69(10)	5(9)	110(10)
O(2A)	250(12)	251(12)	326(13)	7(10)	87(10)	-93(9)
O(3A)	227(11)	230(12)	283(13)	-18(9)	60(9)	85(9)
O(4A)	278(11)	104(11)	218(12)	6(9)	-49(9)	-5(8)
B(1A)	360(20)	103(17)	206(19)	33(14)	8(16)	-38(15)
C(1A)	159(15)	201(16)	112(14)	-41(12)	-8(11)	-10(12)
C(2A)	175(15)	181(16)	140(15)	1(12)	-7(12)	49(12)
C(3A)	203(15)	123(14)	145(14)	-16(11)	20(12)	-29(12)
C(4A)	224(15)	148(15)	112(14)	-18(11)	42(12)	9(12)
C(5A)	140(14)	147(15)	102(14)	-30(11)	-11(11)	21(11)
C(6A)	182(15)	151(15)	164(15)	-11(12)	24(12)	8(11)
C(7A)	170(15)	255(18)	221(17)	-44(13)	44(13)	-11(12)
C(8A)	187(16)	254(18)	231(17)	-14(13)	-16(13)	93(13)
C(9A)	284(17)	172(16)	304(18)	38(14)	37(14)	58(13)
C(10A)	163(15)	192(16)	242(17)	9(13)	7(12)	-2(12)
C(11A)	117(13)	123(14)	166(15)	-36(11)	53(11)	-16(11)
C(12A)	165(14)	158(16)	204(16)	-12(12)	48(12)	12(11)
C(13A)	199(15)	124(15)	305(18)	-18(13)	79(13)	13(12)
C(14A)	190(15)	164(16)	288(18)	-104(13)	76(13)	-26(12)
C(15A)	204(15)	236(17)	178(16)	-95(13)	46(12)	-24(12)
C(16A)	189(15)	159(16)	199(16)	-19(12)	60(12)	-2(11)

C(17A)	171(14)	99(14)	184(15)	-11(11)	63(12)	9(11)
C(18A)	220(15)	181(16)	206(16)	-7(12)	52(13)	-41(12)
C(19A)	345(18)	182(16)	191(16)	6(13)	98(14)	-17(13)
C(20A)	266(17)	185(16)	318(18)	25(14)	162(14)	11(13)
C(21A)	161(15)	162(16)	362(19)	10(14)	109(13)	45(12)
C(22A)	155(14)	178(16)	232(16)	15(12)	60(12)	62(12)
C(23A)	131(14)	156(15)	116(14)	-27(11)	-13(11)	15(11)
C(24A)	187(15)	188(16)	252(17)	-22(13)	62(13)	10(12)
C(25A)	174(16)	300(20)	342(19)	-53(15)	98(14)	-42(13)
C(26A)	174(16)	320(20)	331(19)	-104(15)	83(14)	60(13)
C(27A)	218(16)	193(16)	242(17)	-37(13)	6(13)	58(12)
C(28A)	159(14)	199(16)	153(15)	-26(12)	5(11)	3(12)
C(29A)	111(13)	116(15)	193(15)	32(11)	41(11)	8(10)
C(30A)	164(14)	161(16)	213(16)	14(13)	3(12)	5(12)
C(31A)	195(15)	123(15)	350(19)	41(13)	43(14)	6(12)
C(32A)	263(17)	204(17)	315(19)	137(14)	99(14)	43(13)
C(33A)	345(18)	310(20)	212(17)	105(14)	93(14)	58(14)
C(34A)	242(16)	177(16)	211(16)	-5(13)	53(13)	14(12)
C(35A)	144(14)	123(14)	121(14)	23(11)	15(11)	3(11)
C(36A)	190(15)	174(15)	208(16)	-20(12)	42(12)	0(12)
C(37A)	145(14)	233(17)	227(17)	8(13)	35(12)	18(12)
C(38A)	146(14)	199(16)	181(16)	56(12)	-25(12)	-45(12)
C(39A)	240(16)	136(15)	142(15)	-16(11)	1(12)	-24(12)
C(40A)	170(14)	187(15)	142(14)	11(12)	25(11)	4(11)
C(41A)	480(20)	159(17)	255(18)	6(13)	-14(16)	25(14)
C(42A)	690(30)	254(19)	173(17)	11(14)	-38(17)	30(17)
C(43A)	408(19)	168(16)	197(16)	17(13)	51(14)	-105(14)
C(44A)	376(19)	262(18)	292(19)	33(15)	36(15)	-73(15)
C(45A)	314(18)	146(16)	273(18)	3(13)	50(14)	-47(13)

C(46A)	430(20)	201(18)	420(20)	-37(15)	116(17)	-2(15)
Re(2)	120(1)	100(1)	123(1)	2(1)	42(1)	10(1)
P(1B)	139(3)	117(4)	133(4)	0(3)	46(3)	3(3)
P(2B)	136(4)	124(4)	137(4)	15(3)	47(3)	24(3)
O(1B)	168(11)	239(12)	220(11)	19(9)	53(9)	-52(9)
O(2B)	254(12)	220(12)	347(14)	-6(10)	95(10)	100(9)
O(3B)	215(11)	236(12)	338(13)	15(10)	97(10)	-58(9)
O(4B)	146(10)	127(11)	251(11)	-8(8)	67(8)	35(8)
B(1B)	220(18)	81(16)	244(19)	-13(13)	30(15)	68(13)
C(1B)	226(16)	117(15)	143(15)	16(11)	47(12)	77(12)
C(2B)	190(15)	165(15)	153(15)	-18(12)	82(12)	-21(12)
C(3B)	180(15)	166(15)	151(15)	6(12)	52(12)	62(12)
C(4B)	129(14)	188(16)	98(14)	9(11)	29(11)	8(11)
C(5B)	137(14)	178(15)	133(14)	46(12)	22(11)	11(11)
C(6B)	213(15)	171(16)	241(17)	30(13)	88(13)	12(12)
C(7B)	225(16)	318(19)	350(20)	56(15)	156(14)	53(14)
C(8B)	206(16)	310(20)	380(20)	127(16)	108(15)	-17(14)
C(9B)	231(16)	214(17)	286(18)	73(14)	32(14)	-56(13)
C(10B)	193(15)	185(16)	182(16)	26(12)	26(12)	2(12)
C(11B)	167(14)	141(15)	182(15)	-30(12)	85(12)	-6(11)
C(12B)	148(14)	154(15)	216(16)	-25(12)	48(12)	-4(11)
C(13B)	178(15)	143(16)	340(19)	-46(13)	79(13)	14(12)
C(14B)	262(17)	257(19)	324(19)	-160(15)	106(14)	-24(14)
C(15B)	372(19)	350(20)	175(17)	-87(15)	48(14)	-10(15)
C(16B)	350(18)	192(16)	191(16)	-1(13)	69(14)	21(13)
C(17B)	132(13)	133(15)	131(14)	-35(11)	6(11)	-4(11)
C(18B)	171(14)	196(16)	188(15)	20(12)	46(12)	4(12)
C(19B)	147(14)	251(17)	196(16)	-13(13)	40(12)	-11(12)

C(20B)	197(15)	177(16)	188(16)	-42(12)	-15(12)	66(12)
C(21B)	253(16)	147(15)	157(15)	8(12)	2(12)	39(12)
C(22B)	191(15)	153(15)	160(15)	7(12)	61(12)	1(11)
C(23B)	142(14)	184(16)	84(13)	18(11)	26(11)	-2(11)
C(24B)	160(14)	228(17)	166(15)	10(12)	44(12)	41(12)
C(25B)	99(14)	370(20)	182(16)	11(14)	24(12)	6(13)
C(26B)	172(16)	390(20)	187(16)	13(14)	32(13)	-120(14)
C(27B)	290(17)	221(17)	215(17)	-18(13)	77(13)	-75(13)
C(28B)	199(15)	199(16)	194(16)	14(12)	68(12)	14(12)
C(29B)	155(14)	174(16)	222(16)	47(13)	97(12)	46(12)
C(30B)	142(14)	210(17)	246(17)	24(13)	89(12)	25(12)
C(31B)	184(15)	179(17)	420(20)	75(14)	147(14)	13(12)
C(32B)	295(18)	229(18)	380(20)	177(15)	169(15)	89(14)
C(33B)	328(18)	350(20)	250(18)	124(15)	95(15)	113(15)
C(34B)	329(18)	190(17)	224(17)	39(13)	75(14)	61(13)
C(35B)	151(14)	124(15)	155(14)	34(11)	57(11)	25(11)
C(36B)	225(15)	120(15)	200(16)	-20(12)	62(12)	-10(11)
C(37B)	158(15)	225(17)	248(17)	-12(13)	62(13)	36(12)
C(38B)	241(16)	190(16)	228(16)	-5(13)	149(13)	22(12)
C(39B)	236(16)	187(16)	138(14)	-9(12)	67(12)	1(12)
C(40B)	161(14)	171(15)	164(15)	27(12)	41(12)	23(11)
C(41B)	357(19)	147(16)	450(20)	21(15)	172(16)	52(14)
C(42B)	420(20)	219(19)	890(30)	0(20)	300(20)	-47(16)
C(43B)	221(16)	134(15)	288(18)	-48(13)	7(13)	30(12)
C(44B)	248(18)	298(19)	530(20)	-41(17)	151(16)	37(14)
C(45B)	282(17)	180(16)	270(18)	-53(13)	-21(14)	68(13)
C(46B)	390(20)	223(18)	267(18)	-95(14)	-63(15)	91(14)
C(51C)	540(20)	340(20)	340(20)	-66(17)	124(18)	83(18)

C(52C)	620(30)	500(30)	620(30)	30(20)	200(20)	220(20)
C(53C)	890(40)	490(30)	730(30)	40(20)	450(30)	30(20)
C(54C)	580(30)	350(20)	730(30)	140(20)	370(20)	70(20)
C(55C)	890(30)	500(30)	640(30)	-90(20)	430(30)	120(20)
C(56C)	380(20)	300(20)	430(20)	-14(17)	140(17)	36(16)
C(57C)	550(30)	680(30)	590(30)	-190(20)	260(20)	-110(20)
C(51D)	333(19)	258(18)	252(18)	97(14)	-29(15)	-64(14)
C(52D)	350(20)	380(20)	289(19)	27(16)	69(16)	-114(16)
C(53D)	420(20)	460(20)	310(20)	-45(17)	19(17)	-140(17)
C(54D)	310(20)	460(20)	400(20)	16(18)	9(17)	-7(17)
C(55D)	300(20)	340(20)	710(30)	80(20)	40(20)	-17(17)
C(56D)	300(20)	217(19)	600(30)	0(17)	-73(18)	-23(15)
C(57D)	490(20)	340(20)	280(20)	16(16)	58(17)	-57(17)

Table 1. Crystal data and structure refinement for [1-M_2][BAr^F_4] (AJMM43) (CCDC 768445).

Empirical formula	$[C_{46}H_{52}B_2O_4P_2Re]^+ [C_{24}BF_{20}]^- \bullet C_2H_4Cl_2$
Formula weight	1716.64
Crystallization Solvent	Dichloroethane
Crystal Habit	Block
Crystal size	0.26 x 0.21 x 0.14 mm^3
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 9721 reflections used in lattice determination	2.45 to 35.44°	
Unit cell dimensions	a = 16.0785(8) Å	
	b = 19.3393(9) Å	β= 90.578(2)°
	c = 22.2924(10) Å	
Volume	6931.4(6) $Å^3$	
Z	4	
Crystal system	Monoclinic	
Space group	P $2_1/n$	
Density (calculated)	1.645 Mg/m^3	
F(000)	3416	
θ range for data collection	1.88 to 36.56°	

Completeness to $\theta = 36.56°$	86.5 %
Index ranges	$-23 \le h \le 25, -28 \le k \le 31, -36 \le l \le 36$
Data collection scan type	ω scans; 14 settings
Reflections collected	178979
Independent reflections	29574 [R_{int}= 0.0343]
Absorption coefficient	1.980 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7471 and 0.6373

Table 1 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	29574 / 117 / 983
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	2.971
Final R indices [I>2σ(I), 24164 reflections]	R1 = 0.0371, *w*R2 = 0.0708
R indices (all data)	R1 = 0.0515, *w*R2 = 0.0713
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.005
Average shift/error	0.000
Largest diff. peak and hole	4.938 and -2.452 e.Å^{-3}

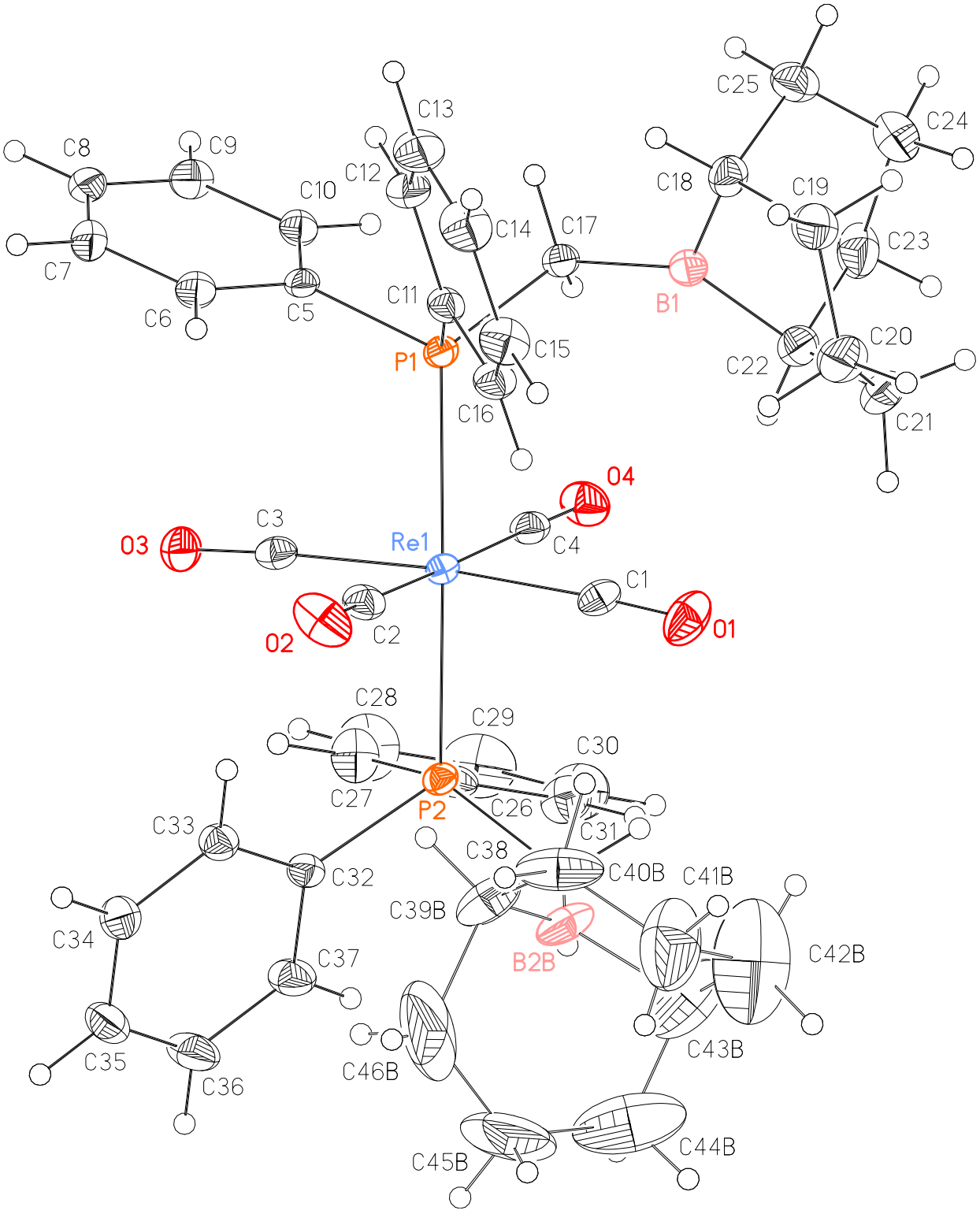
Special Refinement Details

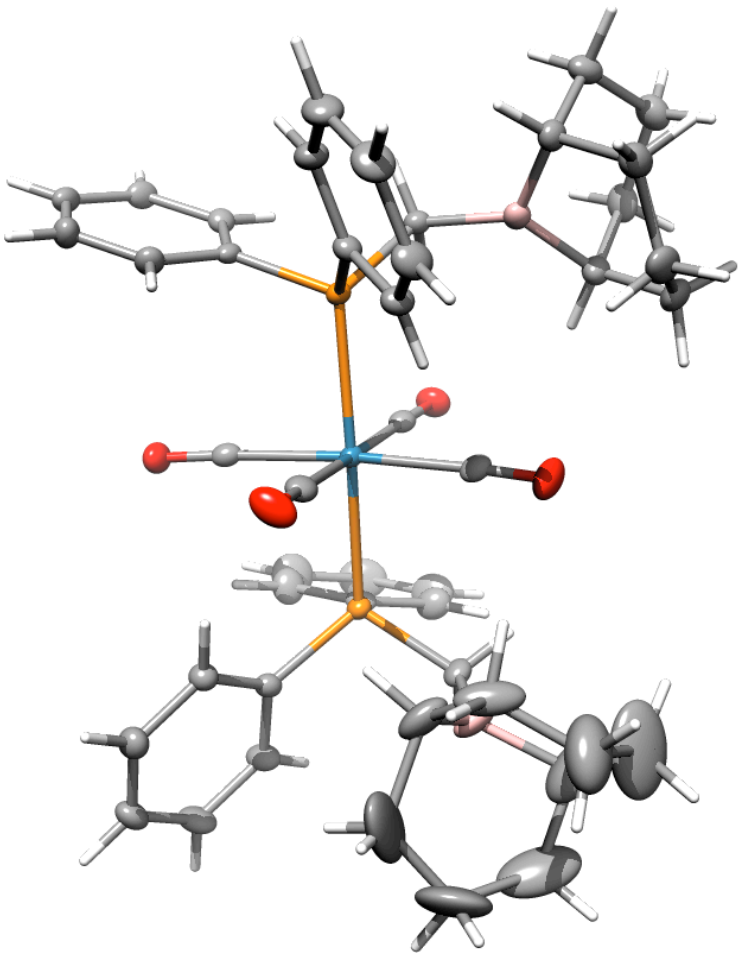
Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

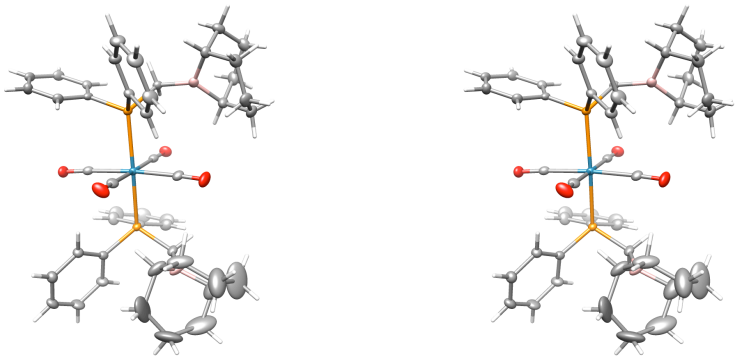
One of the borabicylcononane ligands is disordered by a rotation around the B-C bond. Both the minor (34%) and major (66%) components were restrained to the same geometry as the ordered ligand. The minor component was refined as isotropic and the major component was refined as anisotropic but was restrained to simulate isotropic behavior. The dichloroethane solvent of crystallization was also disordered with both orientations apparently sharing one common Cl site and the ethyl portion flipped about the approximated Cl-Cl vector. The minor component (34%) was refined isotropically and the major component (66%) anisotropically; no geometry restraints were imposed.

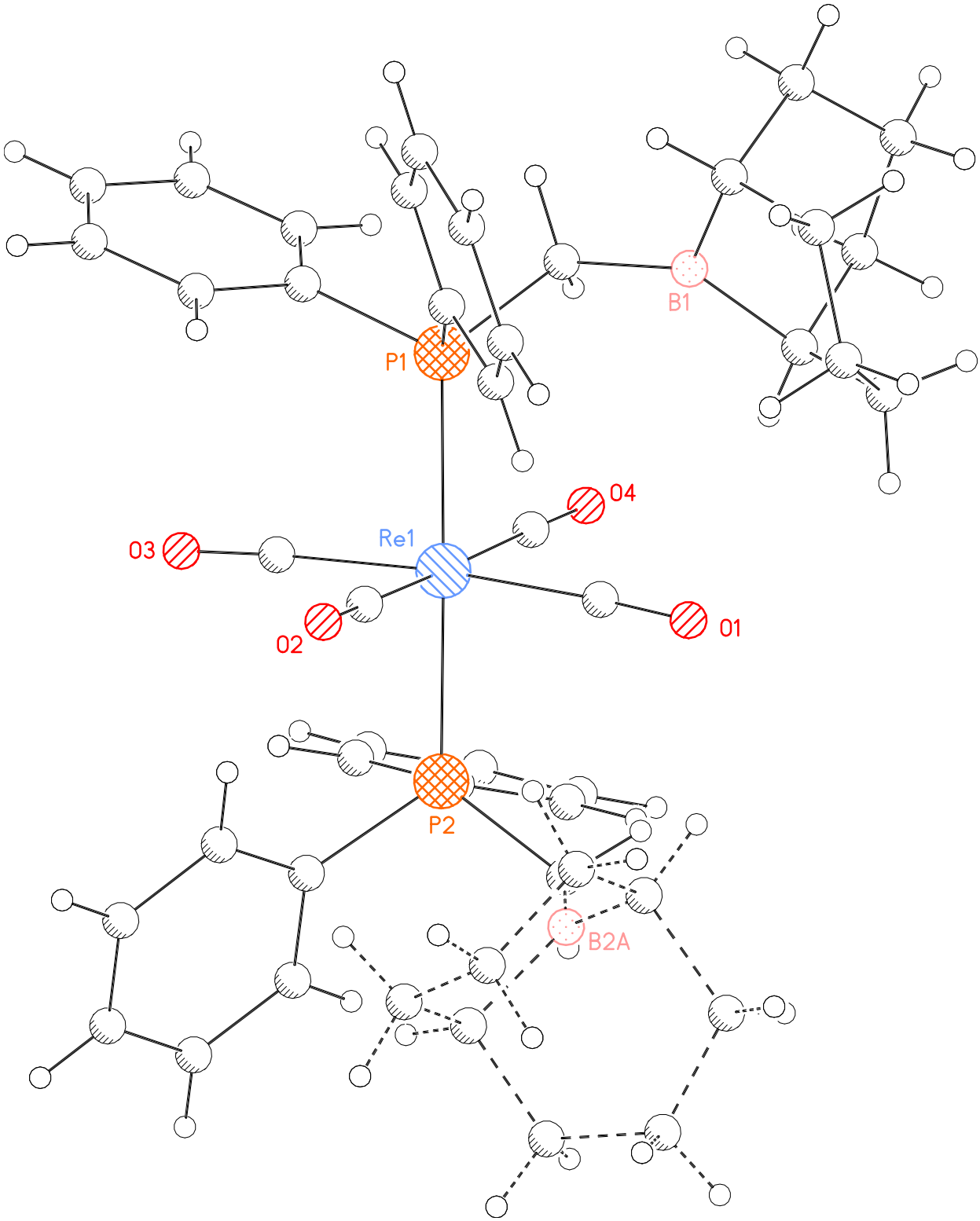
Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

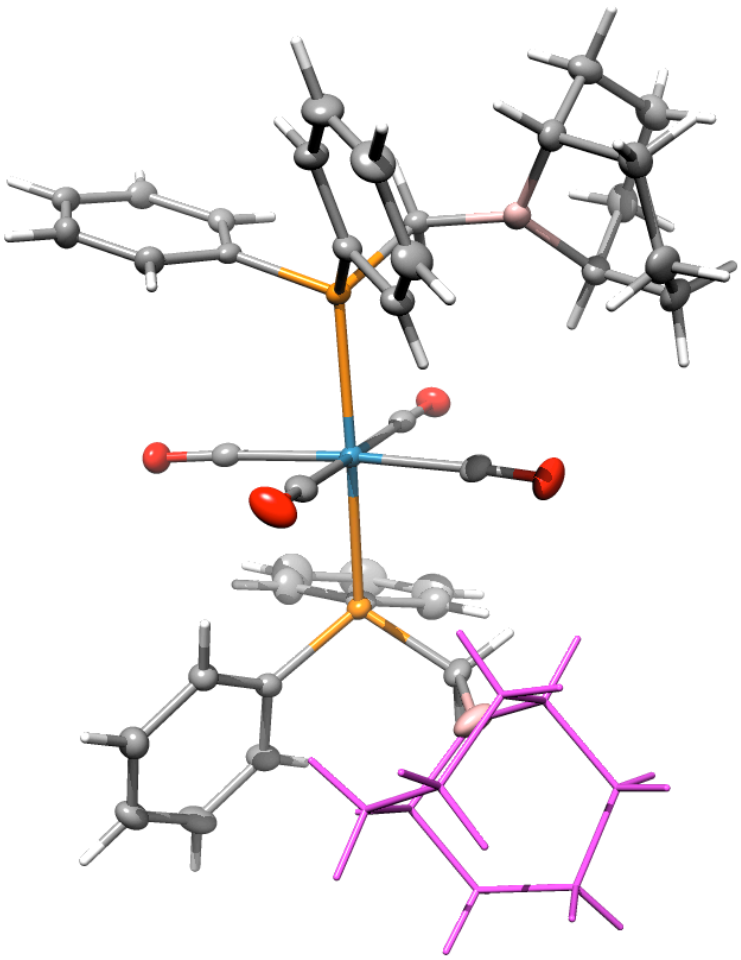
All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

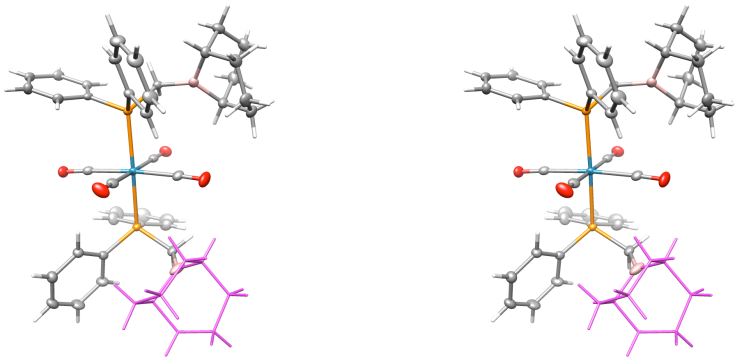

C25
C24
C13
C8
C9
C12
C18
C19
C10
C14
C17
C23
C7
B1
C11
C5
C6
C20
P1
C15
C22
C16
C21
04
C3
03
Re1
C4
C1
C2
02
01
C28
C29
C30
C27
P2
C26
C31
C33
C38
C40B
C41B
C32
C39B
B2B
C42B
C34
C37
C43B
C35
C46B
C36
C44B
C45B

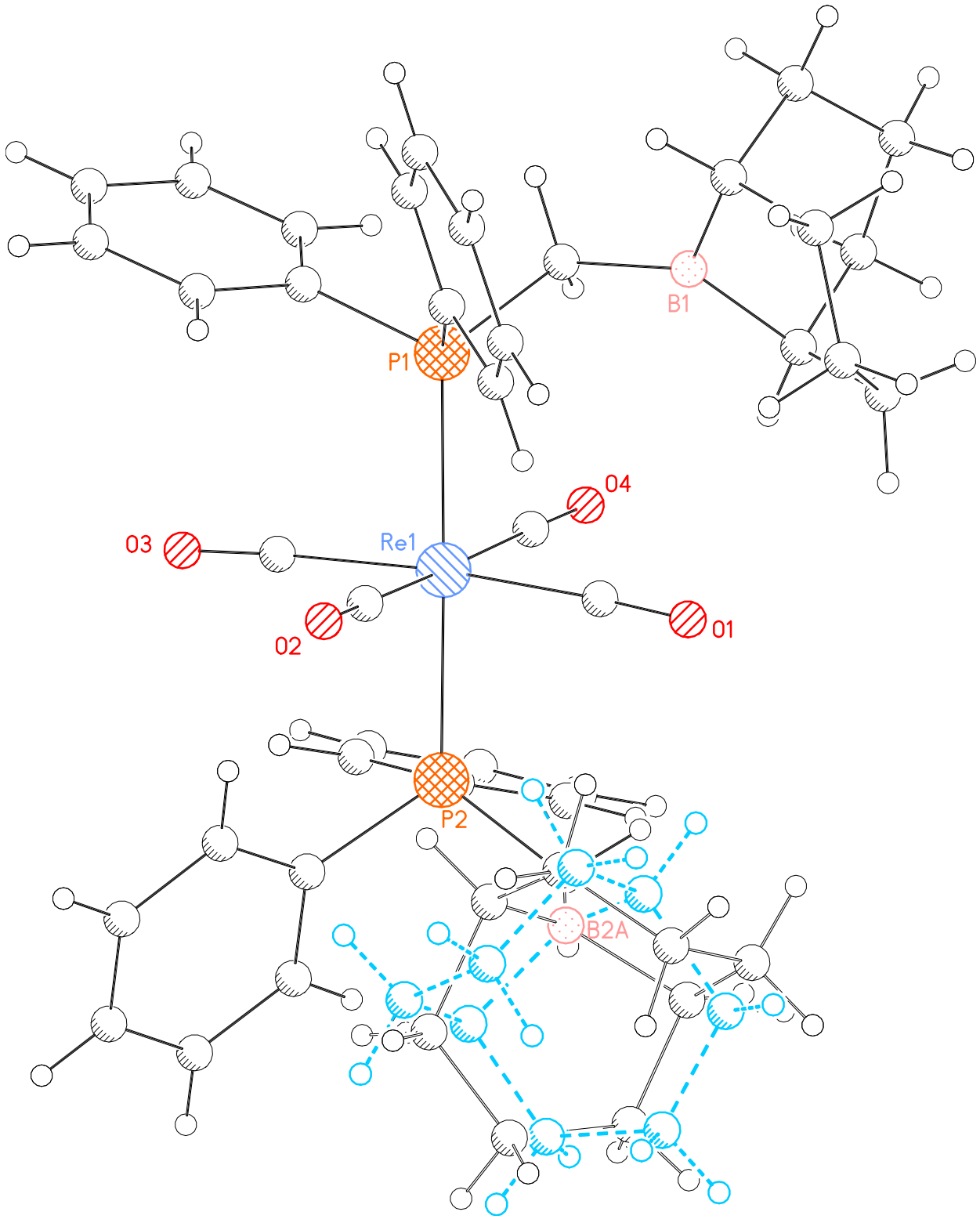


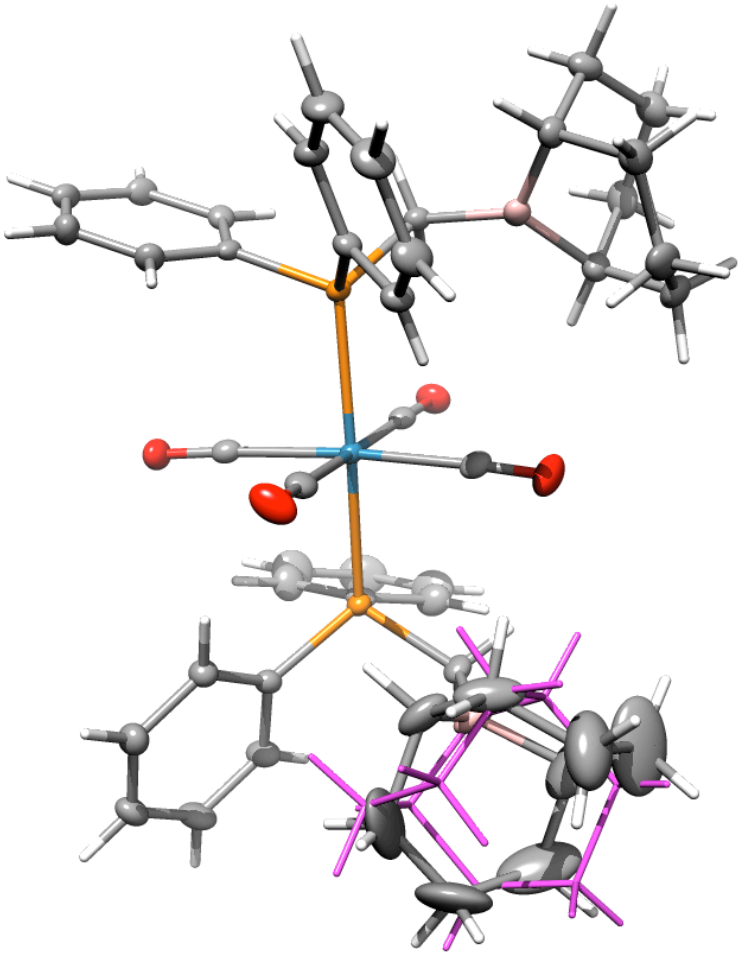


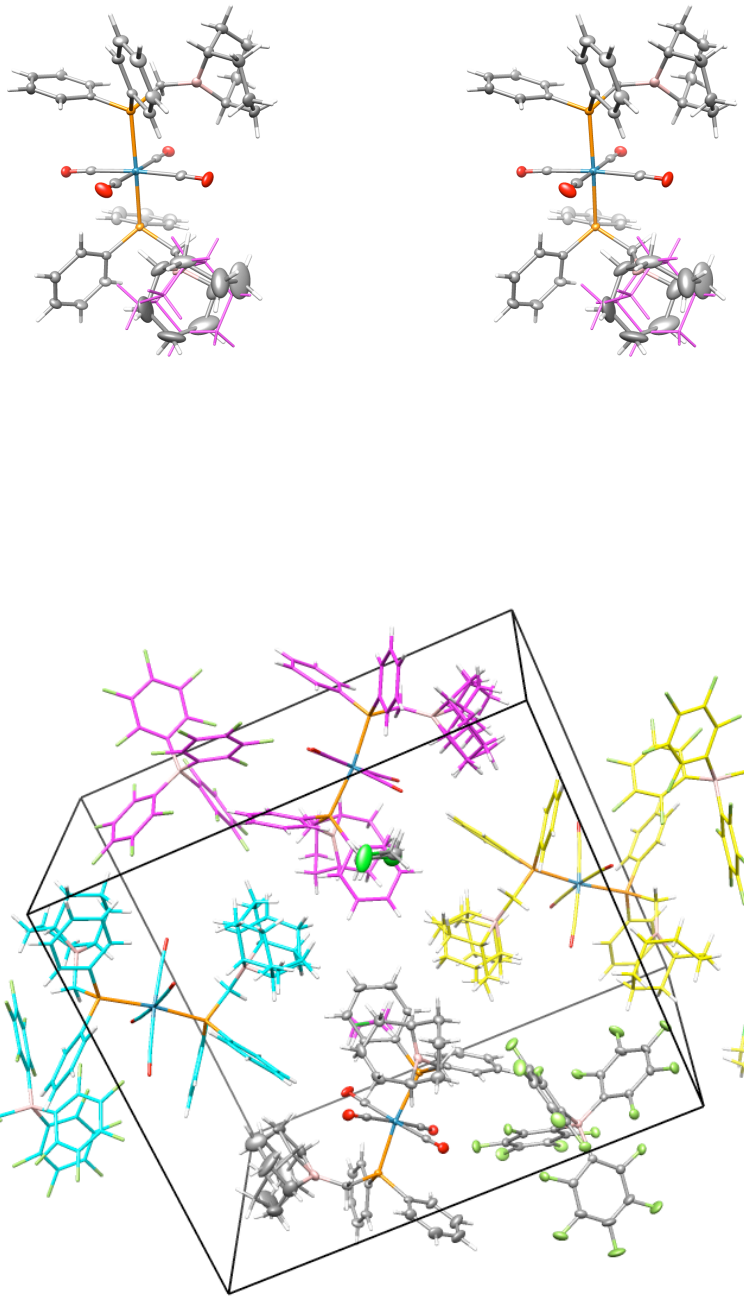

P1
B1
Re1
04
03
02
01
P2
B2A






P1
B1
04
03
Re1
02
01
P2
B2A





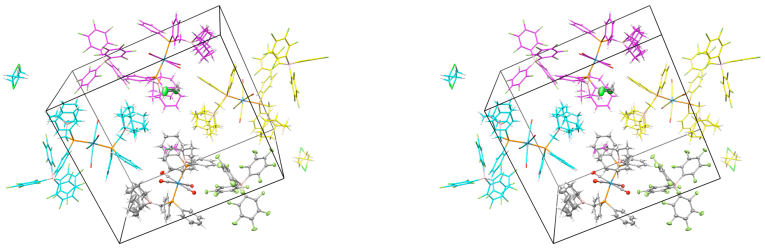


Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [1-M_2][BAr^F_4] (AJMM43) (CCDC 768445). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
Re(1)	2798(1)	8597(1)	5895(1)	13(1)	1
P(1)	3164(1)	7812(1)	5075(1)	14(1)	1
P(2)	2388(1)	9494(1)	6610(1)	15(1)	1
O(1)	1562(1)	7577(1)	6497(1)	32(1)	1
O(2)	4156(1)	7916(1)	6715(1)	32(1)	1
O(3)	4159(1)	9649(1)	5463(1)	24(1)	1
O(4)	1352(1)	9123(1)	5055(1)	26(1)	1
C(1)	2001(2)	7949(1)	6260(1)	20(1)	1
C(2)	3671(2)	8176(1)	6416(1)	20(1)	1
C(3)	3657(1)	9272(1)	5597(1)	18(1)	1
C(4)	1890(2)	8953(1)	5354(1)	18(1)	1
C(5)	3959(1)	8200(1)	4603(1)	16(1)	1
C(6)	4795(2)	8171(1)	4779(1)	21(1)	1
C(7)	5397(2)	8484(1)	4428(1)	25(1)	1
C(8)	5168(2)	8832(1)	3905(1)	23(1)	1
C(9)	4346(2)	8871(1)	3735(1)	21(1)	1
C(10)	3740(1)	8558(1)	4082(1)	18(1)	1
C(11)	3604(1)	6976(1)	5276(1)	17(1)	1
C(12)	4053(2)	6603(1)	4856(1)	23(1)	1
C(13)	4347(2)	5948(1)	4994(1)	30(1)	1
C(14)	4203(2)	5660(1)	5547(1)	30(1)	1
C(15)	3752(2)	6020(1)	5970(1)	27(1)	1
C(16)	3452(2)	6676(1)	5835(1)	21(1)	1
C(17)	2338(1)	7574(1)	4547(1)	17(1)	1

B(1)	1715(2)	6994(1)	4782(1)	20(1)	1
C(18)	1820(2)	6227(1)	4641(1)	22(1)	1
C(19)	1479(2)	5736(1)	5122(1)	28(1)	1
C(20)	1114(2)	6114(1)	5649(1)	36(1)	1
C(21)	493(2)	6662(1)	5487(1)	35(1)	1
C(22)	802(2)	7180(1)	5011(1)	27(1)	1
C(23)	325(2)	7122(1)	4421(1)	32(1)	1
C(24)	400(2)	6407(1)	4123(1)	31(1)	1
C(25)	1282(2)	6187(1)	4040(1)	26(1)	1
C(26)	1853(2)	10193(1)	6209(1)	19(1)	1
C(27)	2319(2)	10675(1)	5892(1)	29(1)	1
C(28)	1918(2)	11175(1)	5544(1)	44(1)	1
C(29)	1061(2)	11200(2)	5516(1)	48(1)	1
C(30)	597(2)	10723(1)	5832(1)	41(1)	1
C(31)	998(2)	10221(1)	6176(1)	30(1)	1
C(32)	3189(1)	9960(1)	7028(1)	17(1)	1
C(33)	3993(1)	9706(1)	7101(1)	19(1)	1
C(34)	4576(2)	10061(1)	7449(1)	24(1)	1
C(35)	4362(2)	10676(1)	7724(1)	26(1)	1
C(36)	3564(2)	10934(1)	7651(1)	30(1)	1
C(37)	2977(2)	10583(1)	7308(1)	25(1)	1
C(38)	1655(1)	9232(1)	7183(1)	21(1)	1
B(2A)	1942(2)	8780(1)	7730(1)	33(1)	0.343(3)
C(39A)	1781(4)	8026(2)	7893(3)	49(2)	0.343(3)
C(40A)	2547(6)	7591(4)	8063(5)	206(13)	0.343(3)
C(41A)	3094(7)	7905(5)	8543(5)	94(4)	0.343(3)
C(42A)	3304(5)	8645(5)	8422(6)	138(8)	0.343(3)
C(43A)	2553(4)	9095(3)	8233(3)	70(4)	0.343(3)
C(44A)	1947(6)	9212(4)	8740(4)	79(5)	0.343(3)

C(45A)	1432(6)	8581(4)	8935(3)	57(3)	0.343(3)
C(46A)	1167(5)	8106(5)	8443(3)	62(4)	0.343(3)
B(2B)	1942(2)	8780(1)	7730(1)	33(1)	0.657(3)
C(39B)	2744(2)	8403(2)	7893(1)	40(1)	0.657(3)
C(40B)	2638(3)	7641(2)	8069(2)	49(2)	0.657(3)
C(41B)	1926(3)	7481(3)	8478(3)	78(2)	0.657(3)
C(42B)	1118(3)	7809(2)	8301(3)	106(3)	0.657(3)
C(43B)	1169(2)	8586(2)	8145(2)	67(2)	0.657(3)
C(44B)	1400(3)	9042(3)	8674(2)	86(2)	0.657(3)
C(45B)	2319(3)	9066(4)	8871(2)	87(2)	0.657(3)
C(46B)	2998(4)	8869(3)	8453(2)	119(3)	0.657(3)

B(3)	1787(2)	9973(1)	2479(1)	15(1)	1
F(1)	3560(1)	9472(1)	2231(1)	24(1)	1
F(2)	4116(1)	9041(1)	1195(1)	37(1)	1
F(3)	3114(1)	9010(1)	203(1)	34(1)	1
F(4)	1507(1)	9459(1)	289(1)	30(1)	1
F(5)	930(1)	9927(1)	1332(1)	23(1)	1
F(6)	1818(1)	11156(1)	1547(1)	28(1)	1
F(7)	1180(1)	12389(1)	1707(1)	52(1)	1
F(8)	301(1)	12706(1)	2710(1)	60(1)	1
F(9)	53(1)	11699(1)	3553(1)	38(1)	1
F(10)	712(1)	10455(1)	3413(1)	23(1)	1
F(11)	2398(1)	8626(1)	2828(1)	25(1)	1
F(12)	1543(1)	7470(1)	2988(1)	37(1)	1
F(13)	-151(1)	7466(1)	2871(1)	39(1)	1
F(14)	-951(1)	8658(1)	2550(1)	34(1)	1
F(15)	-109(1)	9815(1)	2374(1)	23(1)	1
F(16)	3208(1)	10879(1)	2361(1)	23(1)	1

F(17)	4266(1)	11296(1)	3213(1)	32(1)	1
F(18)	4083(1)	10859(1)	4366(1)	38(1)	1
F(19)	2839(1)	9957(1)	4632(1)	33(1)	1
F(20)	1838(1)	9474(1)	3793(1)	24(1)	1
C(51)	2216(1)	9753(1)	1837(1)	15(1)	1
C(52)	3014(1)	9500(1)	1766(1)	18(1)	1
C(53)	3326(2)	9261(1)	1227(1)	23(1)	1
C(54)	2824(2)	9256(1)	727(1)	24(1)	1
C(55)	2016(2)	9484(1)	769(1)	21(1)	1
C(56)	1729(1)	9723(1)	1317(1)	18(1)	1
C(57)	1287(1)	10718(1)	2465(1)	16(1)	1
C(58)	1379(2)	11250(1)	2054(1)	22(1)	1
C(59)	1058(2)	11906(1)	2127(1)	33(1)	1
C(60)	615(2)	12066(1)	2631(1)	36(1)	1
C(61)	490(2)	11560(1)	3053(1)	27(1)	1
C(62)	827(1)	10915(1)	2965(1)	19(1)	1
C(63)	1189(1)	9295(1)	2616(1)	16(1)	1
C(64)	1562(2)	8663(1)	2763(1)	19(1)	1
C(65)	1129(2)	8057(1)	2849(1)	26(1)	1
C(66)	282(2)	8050(1)	2787(1)	27(1)	1
C(67)	-122(2)	8653(1)	2627(1)	24(1)	1
C(68)	340(1)	9252(1)	2541(1)	19(1)	1
C(69)	2470(1)	10140(1)	3019(1)	15(1)	1
C(70)	3104(1)	10614(1)	2918(1)	18(1)	1
C(71)	3652(2)	10848(1)	3352(1)	22(1)	1
C(72)	3566(2)	10626(1)	3934(1)	25(1)	1
C(73)	2940(2)	10175(1)	4062(1)	22(1)	1
C(74)	2421(1)	9936(1)	3614(1)	18(1)	1

Cl(2)	4306(1)	3070(1)	3839(1)	69(1)	1
Cl(1C)	1876(1)	2234(1)	4081(1)	79(1)	0.661(6)
C(81C)	3264(3)	2757(2)	3663(2)	40(1)	0.661(6)
C(82C)	2941(3)	2492(3)	4239(2)	51(2)	0.661(6)
Cl(1D)	1869(11)	2162(9)	4066(7)	371(11)	0.339(6)
C(81D)	2810(6)	2554(4)	3677(3)	28(2)	0.339(6)
C(82D)	3473(5)	2678(3)	4170(3)	17(2)	0.339(6)

Table 3. Selected bond lengths [Å] and angles [°] for [1-M_2][BAr^F_4] (AJMM43) (CCDC 768445).

Re(1)-C(1)	1.974(2)	C(1)-Re(1)-C(2)	87.49(9)
Re(1)-C(2)	1.988(2)	C(1)-Re(1)-C(4)	89.73(9)
Re(1)-C(4)	2.005(2)	C(2)-Re(1)-C(4)	175.94(8)
Re(1)-C(3)	2.018(2)	C(1)-Re(1)-C(3)	174.73(8)
Re(1)-P(2)	2.4509(5)	C(2)-Re(1)-C(3)	88.56(9)
Re(1)-P(1)	2.4521(5)	C(4)-Re(1)-C(3)	94.40(9)
		C(1)-Re(1)-P(2)	90.07(6)
		C(2)-Re(1)-P(2)	95.88(6)
		C(4)-Re(1)-P(2)	87.07(6)
		C(3)-Re(1)-P(2)	86.86(6)
		C(1)-Re(1)-P(1)	94.39(6)
		C(2)-Re(1)-P(1)	90.54(6)
		C(4)-Re(1)-P(1)	86.73(6)
		C(3)-Re(1)-P(1)	89.14(6)
		P(2)-Re(1)-P(1)	172.342(17)

Table 4. Bond lengths [Å] and angles [°] for [1-M_2][BAr^F_4] (AJMM43) (CCDC 768445).

Re(1)-C(1)	1.974(2)	C(15)-C(16)	1.387(3)
Re(1)-C(2)	1.988(2)	C(17)-B(1)	1.596(3)
Re(1)-C(4)	2.005(2)	B(1)-C(18)	1.525(3)
Re(1)-C(3)	2.018(2)	B(1)-C(22)	1.600(3)
Re(1)-P(2)	2.4509(5)	C(18)-C(19)	1.538(3)
Re(1)-P(1)	2.4521(5)	C(18)-C(25)	1.589(3)
P(1)-C(11)	1.820(2)	C(19)-C(20)	1.508(3)
P(1)-C(17)	1.824(2)	C(20)-C(21)	1.498(3)
P(1)-C(5)	1.825(2)	C(21)-C(22)	1.546(3)
P(2)-C(32)	1.820(2)	C(22)-C(23)	1.520(3)
P(2)-C(38)	1.820(2)	C(23)-C(24)	1.539(3)
P(2)-C(26)	1.829(2)	C(24)-C(25)	1.493(3)
O(1)-C(1)	1.141(3)	C(26)-C(31)	1.378(3)
O(2)-C(2)	1.137(3)	C(26)-C(27)	1.393(3)
O(3)-C(3)	1.130(3)	C(27)-C(28)	1.392(3)
O(4)-C(4)	1.135(3)	C(28)-C(29)	1.380(4)
C(5)-C(10)	1.394(3)	C(29)-C(30)	1.384(4)
C(5)-C(6)	1.397(3)	C(30)-C(31)	1.391(3)
C(6)-C(7)	1.389(3)	C(32)-C(33)	1.390(3)
C(7)-C(8)	1.392(3)	C(32)-C(37)	1.402(3)
C(8)-C(9)	1.375(3)	C(33)-C(34)	1.391(3)
C(9)-C(10)	1.389(3)	C(34)-C(35)	1.385(3)
C(11)-C(12)	1.390(3)	C(35)-C(36)	1.385(4)
C(11)-C(16)	1.399(3)	C(36)-C(37)	1.386(3)
C(12)-C(13)	1.385(3)	C(38)-B(2A)	1.568(3)
C(13)-C(14)	1.377(3)	B(2A)-C(39A)	1.524(3)
C(14)-C(15)	1.383(3)	B(2A)-C(43A)	1.603(3)

C(39A)-C(40A)	1.535(3)	F(10)-C(62)	1.352(2)
C(39A)-C(46A)	1.589(3)	F(11)-C(64)	1.353(3)
C(40A)-C(41A)	1.506(3)	F(12)-C(65)	1.351(3)
C(41A)-C(42A)	1.496(4)	F(13)-C(66)	1.341(2)
C(42A)-C(43A)	1.545(3)	F(14)-C(67)	1.342(3)
C(43A)-C(44A)	1.517(3)	F(15)-C(68)	1.357(2)
C(44A)-C(45A)	1.539(3)	F(16)-C(70)	1.353(2)
C(45A)-C(46A)	1.490(3)	F(17)-C(71)	1.351(2)
C(39B)-C(40B)	1.535(3)	F(18)-C(72)	1.344(2)
C(39B)-C(46B)	1.590(3)	F(19)-C(73)	1.349(2)
C(40B)-C(41B)	1.504(3)	F(20)-C(74)	1.359(2)
C(41B)-C(42B)	1.495(4)	C(51)-C(52)	1.384(3)
C(42B)-C(43B)	1.544(3)	C(51)-C(56)	1.392(3)
C(43B)-C(44B)	1.516(3)	C(52)-C(53)	1.386(3)
C(44B)-C(45B)	1.538(3)	C(53)-C(54)	1.370(3)
C(45B)-C(46B)	1.491(3)	C(54)-C(55)	1.376(3)
B(3)-C(57)	1.650(3)	C(55)-C(56)	1.390(3)
B(3)-C(51)	1.651(3)	C(57)-C(58)	1.386(3)
B(3)-C(69)	1.655(3)	C(57)-C(62)	1.398(3)
B(3)-C(63)	1.656(3)	C(58)-C(59)	1.380(3)
F(1)-C(52)	1.352(2)	C(59)-C(60)	1.372(3)
F(2)-C(53)	1.343(3)	C(60)-C(61)	1.374(3)
F(3)-C(54)	1.349(2)	C(61)-C(62)	1.375(3)
F(4)-C(55)	1.341(2)	C(63)-C(68)	1.375(3)
F(5)-C(56)	1.345(2)	C(63)-C(64)	1.399(3)
F(6)-C(58)	1.351(2)	C(64)-C(65)	1.378(3)
F(7)-C(59)	1.338(3)	C(65)-C(66)	1.366(4)
F(8)-C(60)	1.350(3)	C(66)-C(67)	1.381(3)
F(9)-C(61)	1.349(3)	C(67)-C(68)	1.390(3)

C(69)-C(74)	1.387(3)	C(11)-P(1)-C(5)	103.53(10)
C(69)-C(70)	1.392(3)	C(17)-P(1)-C(5)	104.01(9)
C(70)-C(71)	1.379(3)	C(11)-P(1)-Re(1)	117.47(7)
C(71)-C(72)	1.374(3)	C(17)-P(1)-Re(1)	117.30(7)
C(72)-C(73)	1.365(3)	C(5)-P(1)-Re(1)	110.47(6)
C(73)-C(74)	1.375(3)	C(32)-P(2)-C(38)	103.82(10)
Cl(2)-C(82D)	1.714(7)	C(32)-P(2)-C(26)	102.23(10)
Cl(2)-C(81C)	1.822(5)	C(38)-P(2)-C(26)	104.14(10)
Cl(1C)-C(82C)	1.815(6)	C(32)-P(2)-Re(1)	119.29(7)
C(81C)-C(82C)	1.482(7)	C(38)-P(2)-Re(1)	116.05(7)
Cl(1D)-C(81D)	1.907(17)	C(26)-P(2)-Re(1)	109.48(6)
C(81D)-C(82D)	1.542(11)	O(1)-C(1)-Re(1)	176.7(2)
		O(2)-C(2)-Re(1)	177.7(2)
C(1)-Re(1)-C(2)	87.49(9)	O(3)-C(3)-Re(1)	175.94(18)
C(1)-Re(1)-C(4)	89.73(9)	O(4)-C(4)-Re(1)	176.2(2)
C(2)-Re(1)-C(4)	175.94(8)	C(10)-C(5)-C(6)	119.22(19)
C(1)-Re(1)-C(3)	174.73(8)	C(10)-C(5)-P(1)	120.73(17)
C(2)-Re(1)-C(3)	88.56(9)	C(6)-C(5)-P(1)	119.97(15)
C(4)-Re(1)-C(3)	94.40(9)	C(7)-C(6)-C(5)	119.9(2)
C(1)-Re(1)-P(2)	90.07(6)	C(6)-C(7)-C(8)	120.2(2)
C(2)-Re(1)-P(2)	95.88(6)	C(9)-C(8)-C(7)	120.1(2)
C(4)-Re(1)-P(2)	87.07(6)	C(8)-C(9)-C(10)	120.1(2)
C(3)-Re(1)-P(2)	86.86(6)	C(9)-C(10)-C(5)	120.5(2)
C(1)-Re(1)-P(1)	94.39(6)	C(12)-C(11)-C(16)	118.78(19)
C(2)-Re(1)-P(1)	90.54(6)	C(12)-C(11)-P(1)	119.86(16)
C(4)-Re(1)-P(1)	86.73(6)	C(16)-C(11)-P(1)	121.21(16)
C(3)-Re(1)-P(1)	89.14(6)	C(13)-C(12)-C(11)	120.2(2)
P(2)-Re(1)-P(1)	172.342(17)	C(14)-C(13)-C(12)	120.6(2)
C(11)-P(1)-C(17)	102.38(10)	C(13)-C(14)-C(15)	120.1(2)

C(14)-C(15)-C(16)	119.7(2)	C(34)-C(33)-C(32)	120.8(2)
C(15)-C(16)-C(11)	120.6(2)	C(35)-C(34)-C(33)	120.1(2)
B(1)-C(17)-P(1)	114.87(14)	C(36)-C(35)-C(34)	119.5(2)
C(18)-B(1)-C(22)	112.87(18)	C(35)-C(36)-C(37)	120.9(2)
C(18)-B(1)-C(17)	123.03(18)	C(36)-C(37)-C(32)	120.0(2)
C(22)-B(1)-C(17)	121.76(18)	B(2A)-C(38)-P(2)	120.97(17)
B(1)-C(18)-C(19)	114.58(17)	C(39A)-B(2A)-C(38)	132.0(3)
B(1)-C(18)-C(25)	99.22(17)	C(39A)-B(2A)-C(43A)	107.6(3)
C(19)-C(18)-C(25)	111.19(18)	C(38)-B(2A)-C(43A)	120.4(3)
C(20)-C(19)-C(18)	112.85(18)	B(2A)-C(39A)-C(40A)	116.4(5)
C(21)-C(20)-C(19)	114.8(2)	B(2A)-C(39A)-C(46A)	101.5(4)
C(20)-C(21)-C(22)	114.0(2)	C(40A)-C(39A)-C(46A)	111.5(5)
C(23)-C(22)-C(21)	112.6(2)	C(41A)-C(40A)-C(39A)	114.6(5)
C(23)-C(22)-B(1)	99.46(17)	C(42A)-C(41A)-C(40A)	112.9(5)
C(21)-C(22)-B(1)	112.05(19)	C(41A)-C(42A)-C(43A)	114.3(5)
C(24)-C(23)-C(22)	113.41(19)	C(44A)-C(43A)-C(42A)	112.8(5)
C(25)-C(24)-C(23)	112.8(2)	C(44A)-C(43A)-B(2A)	100.6(4)
C(24)-C(25)-C(18)	113.09(18)	C(42A)-C(43A)-B(2A)	116.6(5)
C(31)-C(26)-C(27)	119.2(2)	C(45A)-C(44A)-C(43A)	116.3(5)
C(31)-C(26)-P(2)	121.28(18)	C(46A)-C(45A)-C(44A)	115.6(5)
C(27)-C(26)-P(2)	119.34(18)	C(45A)-C(46A)-C(39A)	116.8(5)
C(28)-C(27)-C(26)	119.9(3)	C(40B)-C(39B)-C(46B)	111.8(3)
C(29)-C(28)-C(27)	120.4(3)	C(41B)-C(40B)-C(39B)	116.1(3)
C(28)-C(29)-C(30)	119.8(3)	C(42B)-C(41B)-C(40B)	114.7(4)
C(29)-C(30)-C(31)	119.7(3)	C(41B)-C(42B)-C(43B)	115.1(4)
C(26)-C(31)-C(30)	120.9(3)	C(44B)-C(43B)-C(42B)	113.9(4)
C(33)-C(32)-C(37)	118.7(2)	C(45B)-C(44B)-C(43B)	117.9(3)
C(33)-C(32)-P(2)	122.60(16)	C(46B)-C(45B)-C(44B)	121.4(4)
C(37)-C(32)-P(2)	118.64(18)	C(45B)-C(46B)-C(39B)	116.9(3)

C(57)-B(3)-C(51)	114.60(16)	C(59)-C(58)-C(57)	124.2(2)
C(57)-B(3)-C(69)	99.40(16)	F(7)-C(59)-C(60)	119.7(2)
C(51)-B(3)-C(69)	113.64(18)	F(7)-C(59)-C(58)	120.2(2)
C(57)-B(3)-C(63)	114.29(18)	C(60)-C(59)-C(58)	120.1(2)
C(51)-B(3)-C(63)	101.82(16)	F(8)-C(60)-C(59)	120.8(2)
C(69)-B(3)-C(63)	113.73(16)	F(8)-C(60)-C(61)	120.4(2)
C(52)-C(51)-C(56)	113.83(18)	C(59)-C(60)-C(61)	118.8(2)
C(52)-C(51)-B(3)	125.88(18)	F(9)-C(61)-C(60)	120.4(2)
C(56)-C(51)-B(3)	119.73(19)	F(9)-C(61)-C(62)	120.5(2)
F(1)-C(52)-C(51)	121.45(18)	C(60)-C(61)-C(62)	119.1(2)
F(1)-C(52)-C(53)	114.5(2)	F(10)-C(62)-C(61)	115.77(19)
C(51)-C(52)-C(53)	124.1(2)	F(10)-C(62)-C(57)	119.12(18)
F(2)-C(53)-C(54)	120.32(19)	C(61)-C(62)-C(57)	125.1(2)
F(2)-C(53)-C(52)	120.1(2)	C(68)-C(63)-C(64)	113.46(19)
C(54)-C(53)-C(52)	119.6(2)	C(68)-C(63)-B(3)	127.04(19)
F(3)-C(54)-C(53)	120.1(2)	C(64)-C(63)-B(3)	119.11(19)
F(3)-C(54)-C(55)	120.5(2)	F(11)-C(64)-C(65)	116.3(2)
C(53)-C(54)-C(55)	119.39(19)	F(11)-C(64)-C(63)	119.69(19)
F(4)-C(55)-C(54)	120.20(19)	C(65)-C(64)-C(63)	124.0(2)
F(4)-C(55)-C(56)	120.6(2)	F(12)-C(65)-C(66)	120.2(2)
C(54)-C(55)-C(56)	119.2(2)	F(12)-C(65)-C(64)	119.9(2)
F(5)-C(56)-C(55)	116.40(19)	C(66)-C(65)-C(64)	119.9(2)
F(5)-C(56)-C(51)	119.73(18)	F(13)-C(66)-C(65)	120.8(2)
C(55)-C(56)-C(51)	123.9(2)	F(13)-C(66)-C(67)	120.2(2)
C(58)-C(57)-C(62)	112.68(19)	C(65)-C(66)-C(67)	119.0(2)
C(58)-C(57)-B(3)	127.23(19)	F(14)-C(67)-C(66)	120.3(2)
C(62)-C(57)-B(3)	119.03(17)	F(14)-C(67)-C(68)	120.6(2)
F(6)-C(58)-C(59)	114.90(19)	C(66)-C(67)-C(68)	119.1(2)
F(6)-C(58)-C(57)	120.91(19)	F(15)-C(68)-C(63)	120.59(19)

F(15)-C(68)-C(67)	115.0(2)
C(63)-C(68)-C(67)	124.4(2)
C(74)-C(69)-C(70)	113.03(19)
C(74)-C(69)-B(3)	126.65(19)
C(70)-C(69)-B(3)	119.55(17)
F(16)-C(70)-C(71)	115.84(19)
F(16)-C(70)-C(69)	119.65(18)
C(71)-C(70)-C(69)	124.50(19)
F(17)-C(71)-C(72)	119.9(2)
F(17)-C(71)-C(70)	120.8(2)
C(72)-C(71)-C(70)	119.4(2)
F(18)-C(72)-C(73)	121.1(2)
F(18)-C(72)-C(71)	120.3(2)
C(73)-C(72)-C(71)	118.6(2)
F(19)-C(73)-C(72)	119.5(2)
F(19)-C(73)-C(74)	120.0(2)
C(72)-C(73)-C(74)	120.4(2)
F(20)-C(74)-C(73)	115.05(18)
F(20)-C(74)-C(69)	120.96(19)
C(73)-C(74)-C(69)	124.0(2)
C(82D)-Cl(2)-C(81C)	39.1(2)
C(82C)-C(81C)-Cl(2)	104.9(3)
C(81C)-C(82C)-Cl(1C)	105.4(4)
C(82D)-C(81D)-Cl(1D)	106.5(7)
C(81D)-C(82D)-Cl(2)	107.5(5)

Table 5. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for [1-M_2][BAr^F_4] (AJMM43) (CCDC 768445). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Re(1)	135(1)	125(1)	119(1)	2(1)	14(1)	15(1)
P(1)	155(3)	142(3)	138(2)	-8(2)	24(2)	2(2)
P(2)	133(3)	157(3)	147(2)	-13(2)	14(2)	23(2)
O(1)	324(12)	242(9)	401(10)	72(7)	159(8)	-8(8)
O(2)	369(12)	223(9)	372(10)	-10(7)	-176(8)	85(8)
O(3)	251(10)	218(8)	252(8)	8(6)	41(7)	-48(7)
O(4)	255(10)	305(9)	234(8)	-15(7)	-73(7)	47(7)
C(1)	203(13)	183(11)	199(10)	-4(8)	44(8)	59(9)
C(2)	249(14)	145(10)	211(10)	-39(8)	12(9)	8(9)
C(3)	191(13)	189(11)	153(9)	-18(8)	2(8)	51(9)
C(4)	218(13)	163(11)	174(10)	-29(8)	41(8)	5(9)
C(5)	187(12)	134(10)	150(9)	-36(7)	44(8)	-15(8)
C(6)	216(13)	259(12)	151(9)	-5(8)	-2(8)	-18(10)
C(7)	185(13)	342(14)	227(11)	-42(9)	15(9)	-55(10)
C(8)	254(14)	229(11)	197(10)	-48(9)	71(9)	-72(10)
C(9)	292(15)	157(11)	193(10)	26(8)	34(9)	-19(10)
C(10)	187(12)	136(10)	211(10)	-24(8)	9(8)	11(9)
C(11)	180(12)	142(10)	200(10)	-27(8)	-2(8)	7(8)
C(12)	243(14)	217(11)	226(11)	-46(9)	34(9)	23(10)
C(13)	292(16)	232(13)	364(13)	-94(10)	32(11)	73(11)
C(14)	327(16)	163(12)	413(14)	-10(10)	-20(11)	71(10)
C(15)	350(16)	173(12)	297(12)	31(9)	-8(10)	16(10)
C(16)	248(14)	152(10)	217(10)	-16(8)	16(9)	10(9)
C(17)	184(12)	173(10)	154(9)	-17(8)	19(8)	2(9)

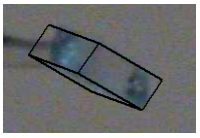
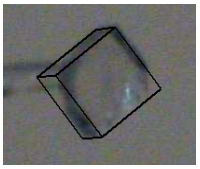
B(1)	208(15)	240(13)	143(10)	-7(9)	8(9)	-36(11)
C(18)	228(14)	197(11)	222(10)	17(8)	38(9)	-26(9)
C(19)	351(16)	235(12)	264(12)	16(10)	33(10)	-62(11)
C(20)	480(20)	359(15)	246(12)	26(11)	123(12)	-146(13)
C(21)	347(17)	375(15)	321(13)	-74(11)	175(11)	-107(12)
C(22)	275(15)	227(12)	302(12)	-60(10)	91(10)	-55(10)
C(23)	212(15)	294(14)	452(15)	-6(11)	15(11)	-2(11)
C(24)	307(16)	283(13)	345(13)	-24(11)	-41(11)	-37(11)
C(25)	356(16)	203(11)	235(11)	-34(9)	12(10)	-30(10)
C(26)	218(13)	171(11)	179(10)	-52(8)	-25(8)	62(9)
C(27)	283(16)	215(12)	366(13)	64(10)	-19(11)	33(10)
C(28)	510(20)	307(15)	510(17)	145(13)	-43(15)	68(14)
C(29)	560(20)	379(16)	485(17)	78(13)	-129(15)	242(15)
C(30)	304(17)	499(18)	439(16)	-24(14)	-91(13)	200(14)
C(31)	251(15)	359(14)	286(12)	4(10)	-17(10)	81(11)
C(32)	191(12)	173(10)	143(9)	-7(8)	-2(8)	-2(9)
C(33)	190(13)	189(11)	202(10)	-24(8)	-1(8)	19(9)
C(34)	193(13)	295(13)	238(11)	-14(9)	-24(9)	6(10)
C(35)	289(15)	263(13)	222(11)	-46(9)	-45(9)	-52(10)
C(36)	358(17)	264(13)	286(12)	-124(10)	-28(11)	20(11)
C(37)	241(14)	262(12)	246(11)	-81(9)	-18(9)	66(10)
C(38)	189(13)	200(11)	233(10)	-22(9)	68(9)	24(9)
B(2A)	430(20)	325(16)	249(13)	16(11)	183(13)	47(14)
B(2B)	430(20)	325(16)	249(13)	16(11)	183(13)	47(14)
C(39B)	430(30)	540(30)	241(19)	104(18)	130(17)	150(20)
C(40B)	790(40)	410(30)	270(20)	-57(18)	-70(20)	360(30)
C(41B)	560(40)	530(30)	1260(50)	80(30)	150(40)	-80(30)
C(42B)	890(50)	670(40)	1600(60)	760(40)	-90(50)	-70(40)
C(43B)	590(40)	720(40)	710(30)	270(30)	250(30)	250(30)

C(44B)	1370(60)	630(40)	580(30)	20(30)	190(40)	610(40)
C(45B)	1110(60)	1130(50)	370(30)	-380(30)	-200(30)	50(40)
C(46B)	1230(60)	1560(60)	790(50)	160(50)	50(50)	-1150(50)

B(3)	136(13)	162(12)	145(10)	21(8)	19(8)	13(9)
F(1)	148(7)	331(7)	232(6)	-79(5)	-30(5)	45(6)
F(2)	199(9)	550(10)	365(8)	-172(7)	64(6)	95(7)
F(3)	405(10)	411(9)	202(7)	-91(6)	86(6)	69(7)
F(4)	402(10)	354(8)	154(6)	-22(5)	-81(6)	76(7)
F(5)	191(8)	303(7)	203(6)	-13(5)	-43(5)	58(6)
F(6)	368(9)	237(7)	224(7)	80(5)	64(6)	18(6)
F(7)	821(15)	248(8)	493(10)	202(7)	130(9)	158(8)
F(8)	825(16)	255(8)	720(12)	30(8)	177(11)	300(9)
F(9)	381(10)	350(8)	424(9)	-102(7)	138(7)	121(7)
F(10)	258(8)	229(7)	215(6)	11(5)	83(5)	5(6)
F(11)	222(8)	211(7)	316(7)	48(5)	-43(6)	36(6)
F(12)	509(11)	171(7)	416(8)	90(6)	-89(7)	-5(7)
F(13)	499(11)	307(8)	369(8)	55(6)	-22(7)	-238(7)
F(14)	198(9)	448(9)	378(8)	-51(6)	30(6)	-128(7)
F(15)	141(7)	254(7)	300(7)	-21(5)	1(5)	37(5)
F(16)	250(8)	236(7)	204(6)	12(5)	41(5)	-66(6)
F(17)	234(9)	309(8)	423(8)	-82(6)	-5(6)	-99(6)
F(18)	398(10)	406(9)	336(8)	-112(6)	-190(7)	-20(7)
F(19)	482(11)	367(8)	150(6)	13(6)	-70(6)	29(7)
F(20)	290(8)	250(7)	170(6)	49(5)	22(5)	-35(6)
C(51)	168(12)	130(10)	156(9)	19(7)	10(8)	-12(8)
C(52)	171(12)	194(11)	174(9)	-16(8)	1(8)	-12(9)
C(53)	167(13)	262(12)	266(11)	-61(9)	60(9)	20(10)
C(54)	326(15)	228(12)	158(9)	-42(9)	67(9)	10(10)

C(55)	286(14)	212(11)	144(9)	4(8)	-25(9)	-15(10)
C(56)	171(12)	182(11)	174(9)	14(8)	6(8)	17(9)
C(57)	123(11)	171(10)	186(9)	2(8)	-16(8)	3(8)
C(58)	227(14)	216(12)	207(10)	17(8)	11(9)	24(9)
C(59)	430(18)	198(12)	358(14)	97(10)	3(12)	65(11)
C(60)	404(18)	198(13)	471(16)	-10(11)	47(13)	145(12)
C(61)	239(15)	258(13)	310(12)	-49(10)	44(10)	64(10)
C(62)	162(12)	192(11)	218(10)	7(8)	0(8)	3(9)
C(63)	169(12)	173(10)	125(9)	-3(8)	18(7)	-16(8)
C(64)	203(13)	204(11)	173(9)	12(8)	-2(8)	-5(9)
C(65)	398(17)	186(12)	196(10)	35(9)	-28(10)	-22(11)
C(66)	373(17)	237(12)	198(11)	23(9)	7(10)	-148(11)
C(67)	190(13)	327(14)	207(10)	-44(9)	37(8)	-75(10)
C(68)	191(13)	201(11)	168(9)	-18(8)	27(8)	2(9)
C(69)	143(12)	151(10)	160(9)	-5(8)	3(8)	34(8)
C(70)	174(12)	172(11)	183(10)	-25(8)	13(8)	26(9)
C(71)	158(13)	170(11)	317(12)	-61(9)	6(9)	-18(9)
C(72)	253(14)	242(12)	240(11)	-97(9)	-106(9)	56(10)
C(73)	298(15)	210(11)	153(10)	-1(8)	-44(9)	62(10)
C(74)	188(13)	165(11)	188(10)	1(8)	2(8)	17(9)
Cl(2)	547(6)	744(6)	766(6)	48(5)	14(5)	33(5)
Cl(1C)	634(11)	953(13)	777(11)	383(8)	-387(8)	-538(9)
C(81C)	410(30)	330(20)	450(30)	-22(19)	-80(20)	30(20)
C(82C)	430(40)	520(30)	590(30)	110(20)	-30(20)	-50(30)

Table 1. Crystal data and structure refinement for [1-M_1][OTf] (AJMM45) (CCDC 779779).

Empirical formula	$[C_{26}H_{26}BO_5PRe]^+ [CF_3O_3S]^-$	
Formula weight	795.52	
Crystallization Solvent	Dichloromethane/pentane	
Crystal Habit	Block	
Crystal size	0.25 x 0.21 x 0.09 mm^3	
Crystal color	Colorless	

Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 9162 reflections used in lattice determination	2.57 to 36.57°	
Unit cell dimensions	a = 17.3374(4) Å	α= 85.9010(10)°
	b = 17.3374(4) Å	β= 85.9010(10)°
	c = 17.3374(4) Å	γ = 85.9010(10)°
Volume	5173.2(2) $Å^3$	
Z	6	
Crystal system	Rhombohedral	
Space group	R -3	
Density (calculated)	1.532 Mg/m^3	
F(000)	2340	
θ range for data collection	1.61 to 37.73°	

Completeness to $\theta = 37.73°$	94.6 %
Index ranges	$-26 \le h \le 29$, $-26 \le k \le 29$, $-29 \le l \le 28$
Data collection scan type	ω scans; 13 settings
Reflections collected	153018
Independent reflections	17454 [R_{int}= 0.0365]
Absorption coefficient	3.687 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8277 and 0.4857

Table 1 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	17454 / 0 / 440
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	2.593
Final R indices [I>2σ(I), 14238 reflections]	R1 = 0.0328, *w*R2 = 0.0541
R indices (all data)	R1 = 0.0432, *w*R2 = 0.0547
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.006
Average shift/error	0.000
Largest diff. peak and hole	3.339 and -3.059 e.Å^{-3}

Special Refinement Details

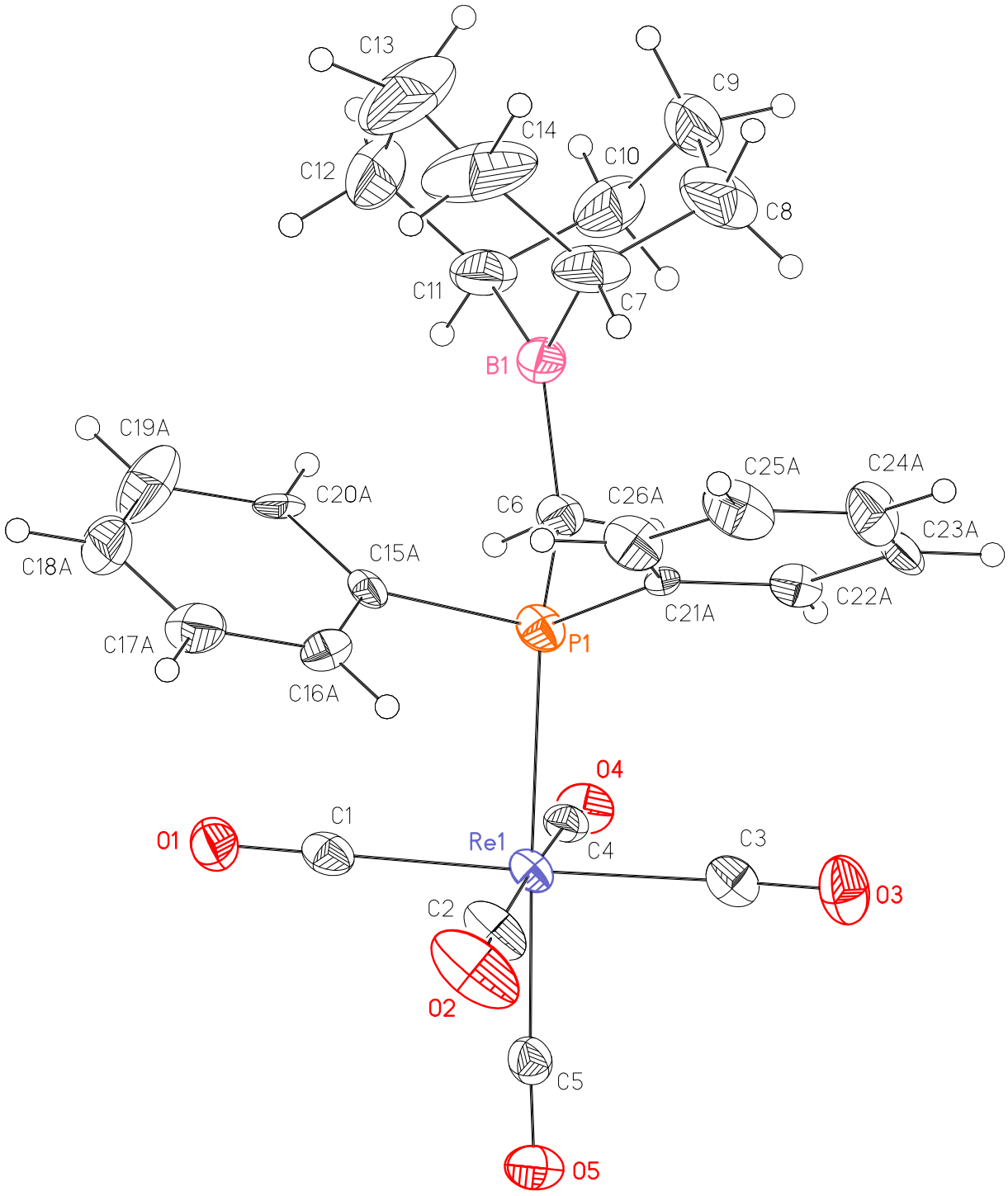
Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

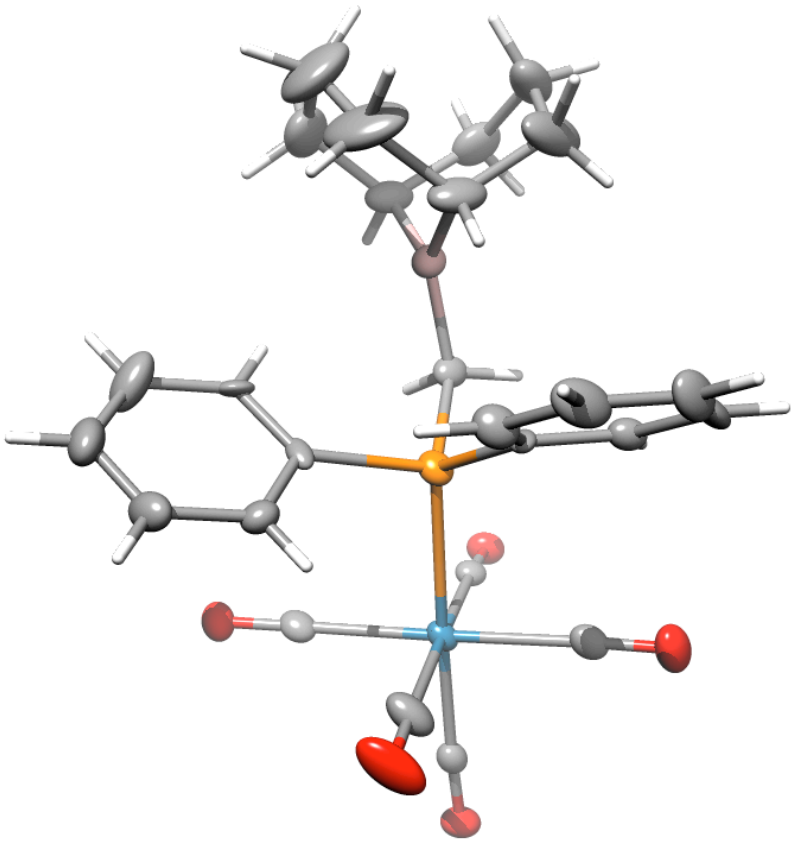
SQUEEZE[19] was used to model disordered solvent(see below). A void near the origin, volume = 867Å^3, presumably filled with dichloromethane and pentane, was accounted for by 309e$^-$. The two phenyl rings are disordered by rotation around the P-C bond. Each was constrained to a regular hexagon.

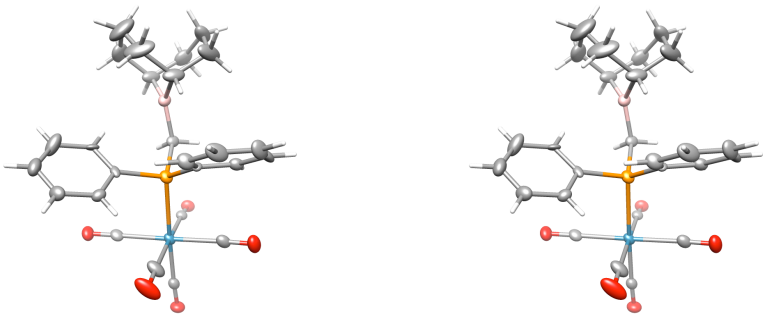
Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement.

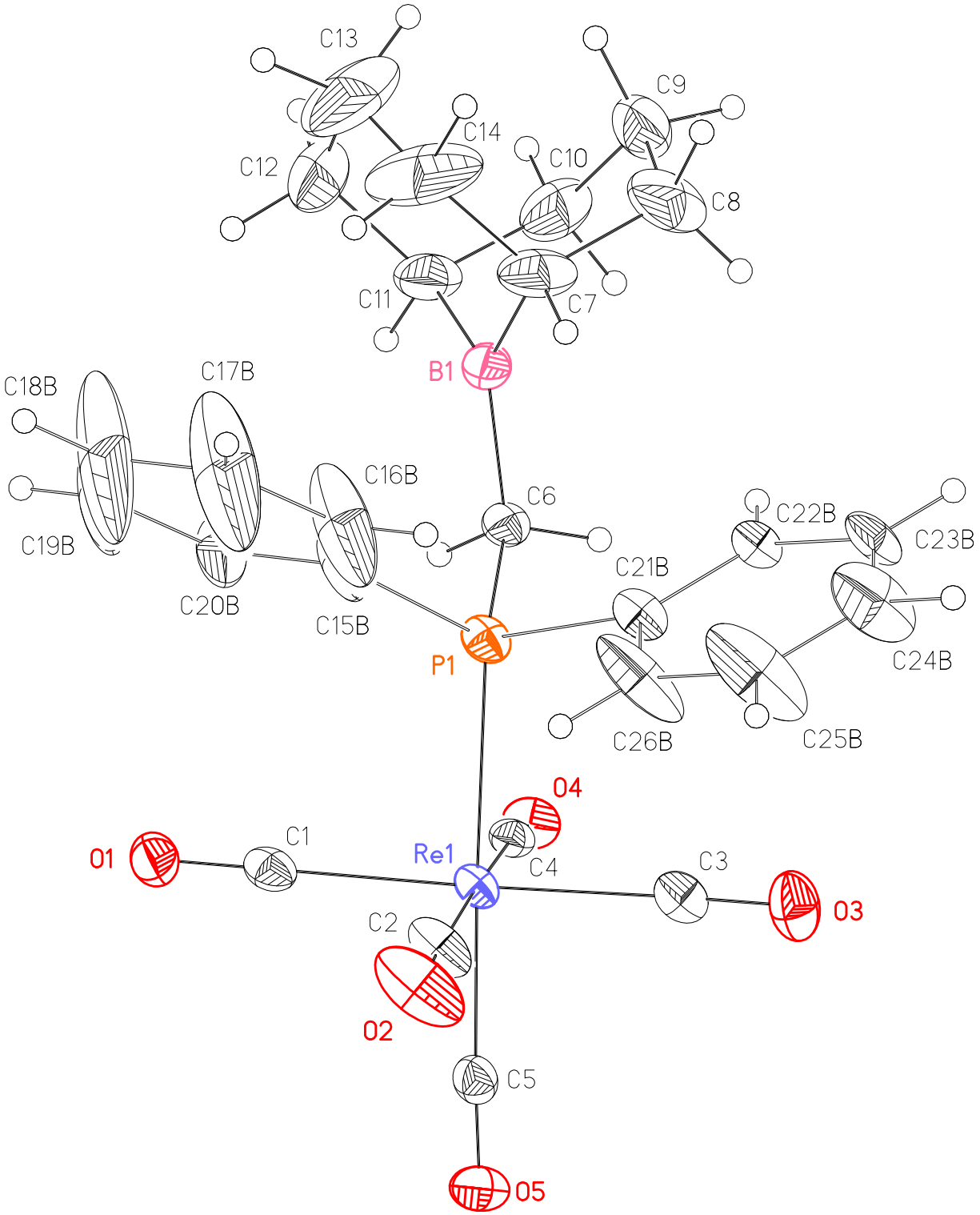
R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

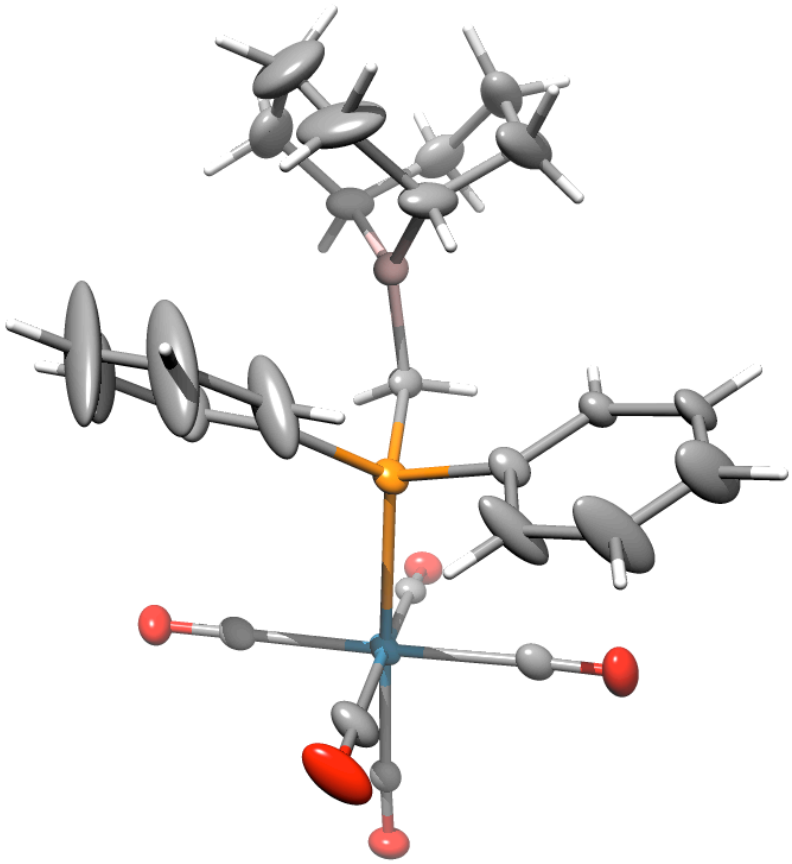
All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

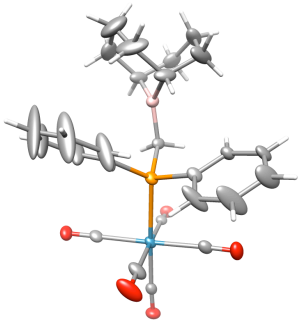

C13
C9
C14
C10
C12
C8
C11
C7
B1
C19A
C20A
C25A
C24A
C6
C26A
C23A
C18A
C15A
C21A
C22A
C17A
P1
C16A
04
C1
01
Re1
C4
C3
03
C2
02
C5
05

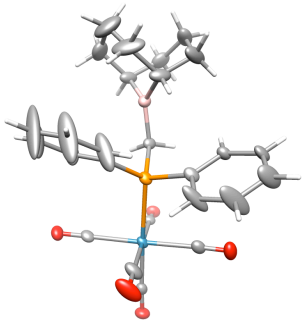


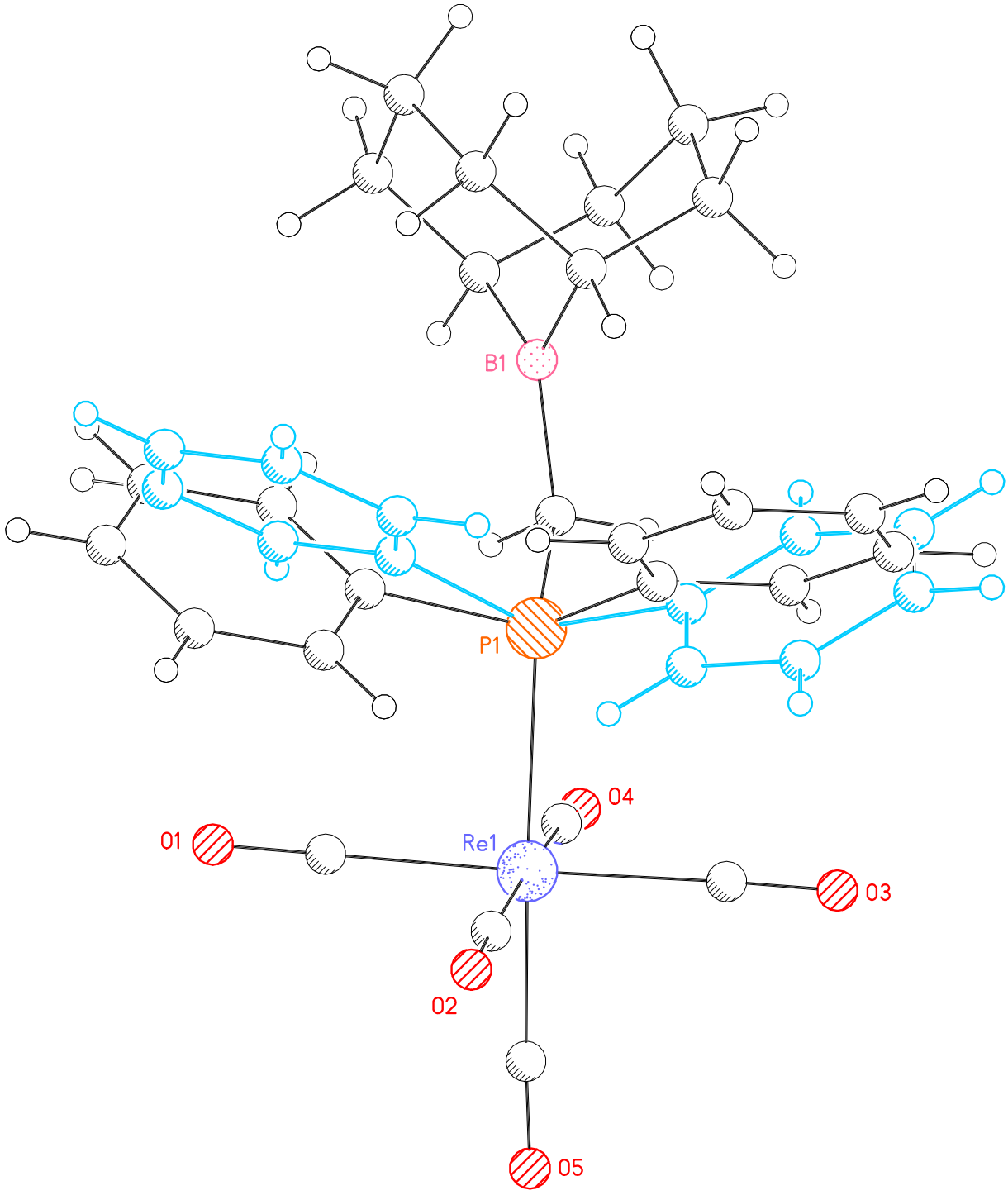


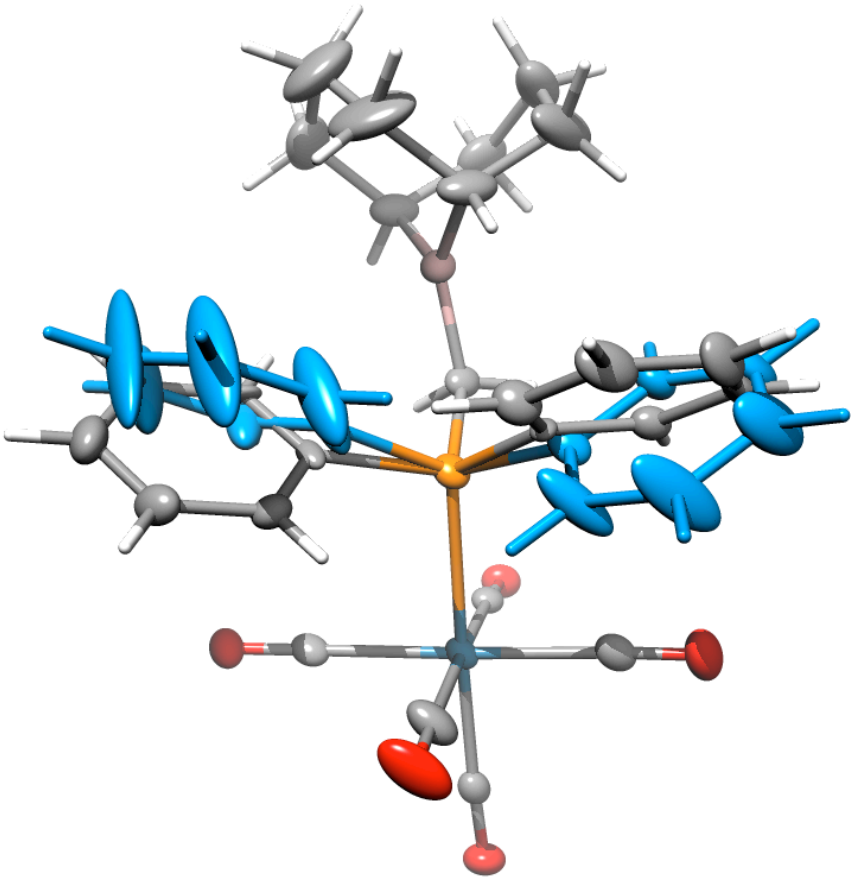

C13
C9
C14
C12
C10
C8
C11
C7
B1
C18B
C17B
C16B
C6
C19B
C22B
C23B
C21B
C20B
C15B
P1
C24B
C26B
C25B
04
01
C1
Re1
C4
C3
03
C2
02
C5
05

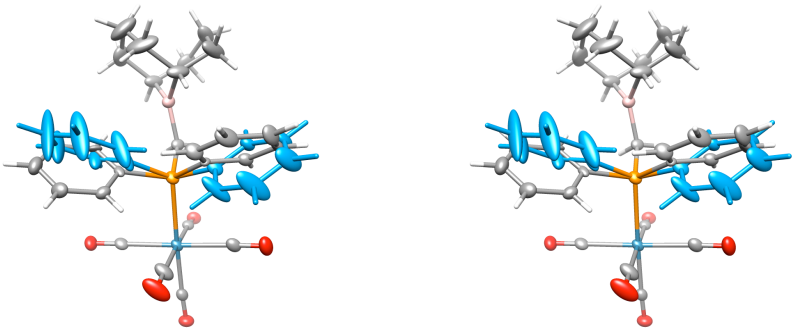


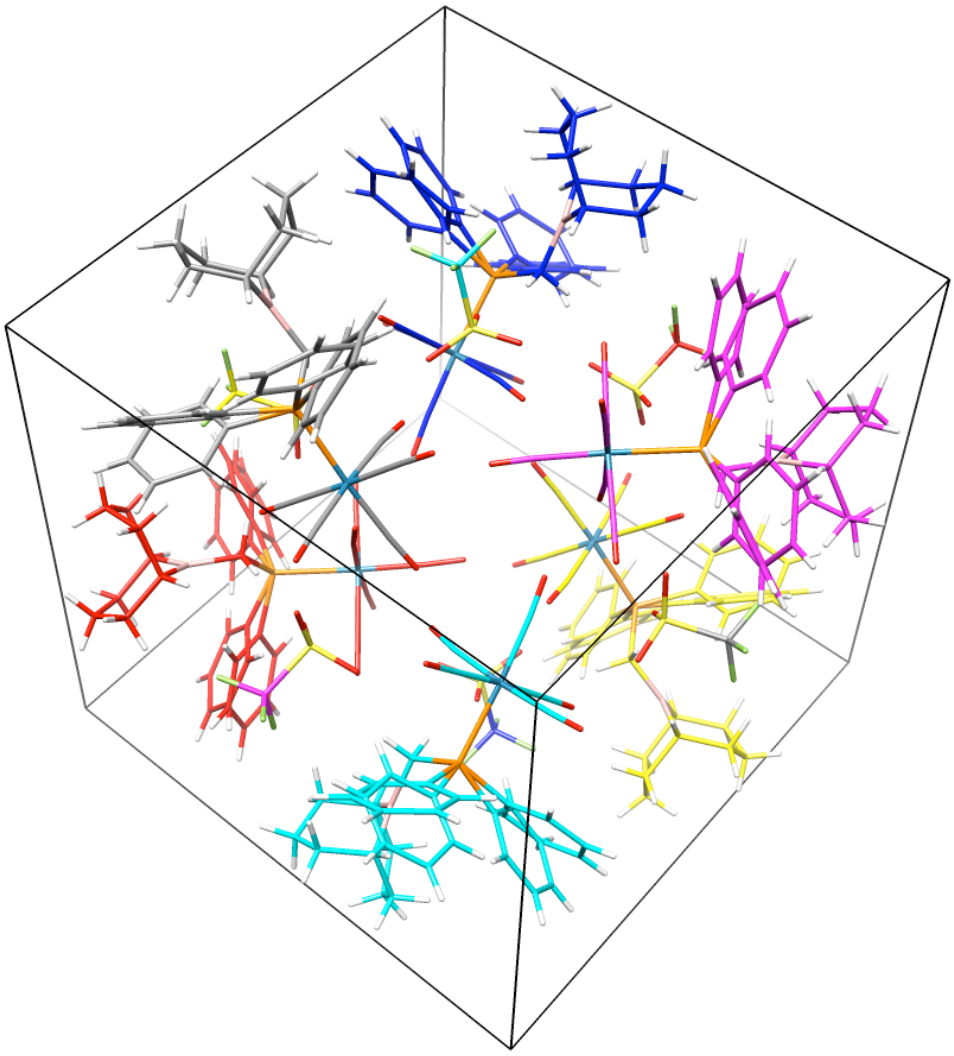





B1
P1
Re1
01
02
03
04
05







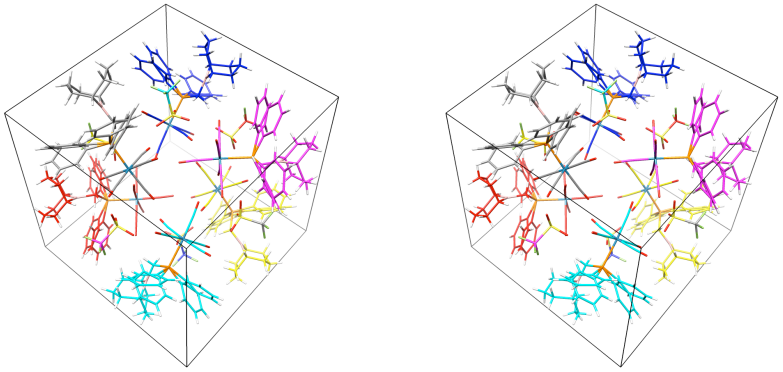


Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [1-M_1][OTf] (AJMM45) (CCDC 779779). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
Re(1)	3232(1)	6057(1)	3009(1)	17(1)	1
P(1)	2116(1)	7035(1)	2933(1)	21(1)	1
O(1)	4341(1)	7337(1)	2316(1)	30(1)	1
O(2)	3122(1)	5574(1)	1315(1)	54(1)	1
O(3)	2062(1)	4807(1)	3598(1)	36(1)	1
O(4)	3517(1)	6401(1)	4718(1)	25(1)	1
O(5)	4600(1)	4831(1)	3254(1)	32(1)	1
B(1)	1369(1)	8316(1)	3775(1)	26(1)	1
C(1)	3949(1)	6880(1)	2576(1)	23(1)	1
C(2)	3150(1)	5762(1)	1925(1)	33(1)	1
C(3)	2478(1)	5264(1)	3401(1)	25(1)	1
C(4)	3381(1)	6309(1)	4107(1)	19(1)	1
C(5)	4110(1)	5280(1)	3138(1)	23(1)	1
C(6)	1948(1)	7581(1)	3792(1)	21(1)	1
C(7)	565(1)	8436(1)	3415(2)	42(1)	1
C(8)	-15(1)	8347(2)	4147(2)	65(1)	1
C(9)	112(2)	8870(2)	4812(2)	58(1)	1
C(10)	952(2)	8899(1)	4976(2)	47(1)	1
C(11)	1511(1)	9008(1)	4265(2)	40(1)	1
C(12)	1401(2)	9784(2)	3810(2)	66(1)	1
C(13)	705(3)	9912(2)	3372(2)	92(1)	1
C(14)	487(2)	9224(2)	2974(2)	82(1)	1
C(15A)	2407(2)	7761(3)	2119(2)	18(1)	0.358(2)

C(16A)	2512(2)	7539(2)	1362(2)	23(1)	0.358(2)
C(17A)	2777(3)	8059(2)	772(2)	33(1)	0.358(2)
C(18A)	2938(3)	8801(2)	939(3)	42(2)	0.358(2)
C(19A)	2834(3)	9023(2)	1696(3)	50(3)	0.358(2)
C(20A)	2569(3)	8503(3)	2286(2)	22(2)	0.358(2)
C(15B)	2139(2)	7789(2)	2172(2)	44(1)	0.642(2)
C(16B)	1668(2)	7839(2)	1552(2)	91(2)	0.642(2)
C(17B)	1739(2)	8435(3)	976(2)	150(4)	0.642(2)
C(18B)	2281(3)	8981(3)	1020(3)	197(6)	0.642(2)
C(19B)	2752(2)	8931(2)	1640(3)	110(4)	0.642(2)
C(20B)	2681(2)	8335(3)	2216(2)	56(2)	0.642(2)
C(21A)	1213(2)	6700(2)	2709(2)	13(1)	0.358(2)
C(22A)	860(3)	6242(3)	3304(2)	22(1)	0.358(2)
C(23A)	154(3)	5941(3)	3204(2)	30(2)	0.358(2)
C(24A)	-197(2)	6098(3)	2509(3)	33(2)	0.358(2)
C(25A)	156(2)	6556(3)	1914(2)	38(2)	0.358(2)
C(26A)	862(2)	6857(2)	2014(2)	29(1)	0.358(2)
C(21B)	1232(1)	6507(2)	2854(1)	23(1)	0.642(2)
C(22B)	663(2)	6437(2)	3457(1)	23(1)	0.642(2)
C(23B)	44(1)	5985(2)	3390(1)	30(1)	0.642(2)
C(24B)	-7(1)	5603(2)	2719(2)	57(2)	0.642(2)
C(25B)	562(1)	5673(2)	2115(2)	73(2)	0.642(2)
C(26B)	1181(1)	6125(2)	2183(1)	57(2)	0.642(2)
C(41)	5806(1)	618(2)	6182(1)	39(1)	1
F(1)	5360(1)	140(1)	5898(1)	56(1)	1

F(2)	6539(1)	330(1)	6074(1)	63(1)	1
F(3)	5645(1)	607(1)	6949(1)	74(1)	1
O(6)	4878(1)	1820(1)	5966(1)	30(1)	1
O(7)	6232(1)	2010(1)	6106(1)	41(1)	1
O(8)	5849(1)	1512(1)	4933(1)	35(1)	1
S(1)	5677(1)	1604(1)	5746(1)	23(1)	1

Table 3. Selected bond lengths [Å] and angles [°] for [1-M_1][OTf] (AJMM45) (CCDC 779779).

Re(1)-C(5)	1.973(2)	C(5)-Re(1)-C(2)	90.36(8)
Re(1)-C(2)	2.0001(19)	C(5)-Re(1)-C(3)	90.61(8)
Re(1)-C(3)	2.016(2)	C(2)-Re(1)-C(3)	89.93(8)
Re(1)-C(4)	2.0208(17)	C(5)-Re(1)-C(4)	85.82(7)
Re(1)-C(1)	2.027(2)	C(2)-Re(1)-C(4)	176.14(8)
Re(1)-P(1)	2.4846(5)	C(3)-Re(1)-C(4)	90.62(7)
		C(5)-Re(1)-C(1)	91.87(8)
		C(2)-Re(1)-C(1)	88.30(8)
		C(3)-Re(1)-C(1)	176.96(8)
		C(4)-Re(1)-C(1)	91.31(7)
		C(5)-Re(1)-P(1)	176.54(6)
		C(2)-Re(1)-P(1)	92.90(7)
		C(3)-Re(1)-P(1)	88.23(6)
		C(4)-Re(1)-P(1)	90.94(5)
		C(1)-Re(1)-P(1)	89.40(6)

Table 4. Bond lengths [Å] and angles [°] for [1-M_1][OTf] (AJMM45) (CCDC 779779).

Re(1)-C(5)	1.973(2)	C(15A)-C(16A)	1.3900
Re(1)-C(2)	2.0001(19)	C(15A)-C(20A)	1.3900
Re(1)-C(3)	2.016(2)	C(16A)-C(17A)	1.3900
Re(1)-C(4)	2.0208(17)	C(17A)-C(18A)	1.3900
Re(1)-C(1)	2.027(2)	C(18A)-C(19A)	1.3900
Re(1)-P(1)	2.4846(5)	C(19A)-C(20A)	1.3900
P(1)-C(21A)	1.784(3)	C(15B)-C(16B)	1.3900
P(1)-C(15B)	1.790(3)	C(15B)-C(20B)	1.3900
P(1)-C(6)	1.8171(18)	C(16B)-C(17B)	1.3900
P(1)-C(21B)	1.8581(18)	C(17B)-C(18B)	1.3900
P(1)-C(15A)	1.888(4)	C(18B)-C(19B)	1.3900
O(1)-C(1)	1.129(2)	C(19B)-C(20B)	1.3900
O(2)-C(2)	1.134(2)	C(21A)-C(22A)	1.3900
O(3)-C(3)	1.127(2)	C(21A)-C(26A)	1.3900
O(4)-C(4)	1.126(2)	C(22A)-C(23A)	1.3900
O(5)-C(5)	1.130(2)	C(23A)-C(24A)	1.3900
B(1)-C(7)	1.561(3)	C(24A)-C(25A)	1.3900
B(1)-C(11)	1.562(3)	C(25A)-C(26A)	1.3900
B(1)-C(6)	1.565(3)	C(21B)-C(22B)	1.3900
C(7)-C(14)	1.519(4)	C(21B)-C(26B)	1.3900
C(7)-C(8)	1.567(4)	C(22B)-C(23B)	1.3900
C(8)-C(9)	1.553(3)	C(23B)-C(24B)	1.3900
C(9)-C(10)	1.508(4)	C(24B)-C(25B)	1.3900
C(10)-C(11)	1.523(4)	C(25B)-C(26B)	1.3900
C(11)-C(12)	1.518(4)	C(41)-F(1)	1.317(2)
C(12)-C(13)	1.466(4)	C(41)-F(3)	1.338(3)
C(13)-C(14)	1.504(4)	C(41)-F(2)	1.338(3)

C(41)-S(1)	1.824(3)	C(21B)-P(1)-C(15A)	118.58(16)
O(6)-S(1)	1.4405(15)	C(21A)-P(1)-Re(1)	117.00(14)
O(7)-S(1)	1.4341(13)	C(15B)-P(1)-Re(1)	118.86(12)
O(8)-S(1)	1.4376(16)	C(6)-P(1)-Re(1)	113.10(6)
		C(21B)-P(1)-Re(1)	107.62(10)
C(5)-Re(1)-C(2)	90.36(8)	C(15A)-P(1)-Re(1)	105.28(14)
C(5)-Re(1)-C(3)	90.61(8)	C(7)-B(1)-C(11)	111.01(19)
C(2)-Re(1)-C(3)	89.93(8)	C(7)-B(1)-C(6)	128.94(17)
C(5)-Re(1)-C(4)	85.82(7)	C(11)-B(1)-C(6)	119.47(17)
C(2)-Re(1)-C(4)	176.14(8)	O(1)-C(1)-Re(1)	178.14(16)
C(3)-Re(1)-C(4)	90.62(7)	O(2)-C(2)-Re(1)	177.7(2)
C(5)-Re(1)-C(1)	91.87(8)	O(3)-C(3)-Re(1)	177.64(17)
C(2)-Re(1)-C(1)	88.30(8)	O(4)-C(4)-Re(1)	173.94(16)
C(3)-Re(1)-C(1)	176.96(8)	O(5)-C(5)-Re(1)	176.32(18)
C(4)-Re(1)-C(1)	91.31(7)	B(1)-C(6)-P(1)	119.16(14)
C(5)-Re(1)-P(1)	176.54(6)	C(14)-C(7)-B(1)	110.3(2)
C(2)-Re(1)-P(1)	92.90(7)	C(14)-C(7)-C(8)	114.0(3)
C(3)-Re(1)-P(1)	88.23(6)	B(1)-C(7)-C(8)	102.4(2)
C(4)-Re(1)-P(1)	90.94(5)	C(9)-C(8)-C(7)	115.28(19)
C(1)-Re(1)-P(1)	89.40(6)	C(10)-C(9)-C(8)	113.6(2)
C(21A)-P(1)-C(15B)	95.32(17)	C(11)-C(10)-C(9)	115.4(2)
C(21A)-P(1)-C(6)	108.22(15)	C(12)-C(11)-C(10)	114.6(2)
C(15B)-P(1)-C(6)	102.08(16)	C(12)-C(11)-B(1)	112.2(2)
C(21A)-P(1)-C(21B)	12.55(18)	C(10)-C(11)-B(1)	103.42(18)
C(15B)-P(1)-C(21B)	107.66(13)	C(13)-C(12)-C(11)	116.7(2)
C(6)-P(1)-C(21B)	106.84(9)	C(12)-C(13)-C(14)	115.5(3)
C(21A)-P(1)-C(15A)	106.77(19)	C(7)-C(14)-C(13)	117.3(3)
C(15B)-P(1)-C(15A)	14.28(16)	C(16A)-C(15A)-C(20A)	120.0
C(6)-P(1)-C(15A)	105.64(14)	C(16A)-C(15A)-P(1)	120.1(2)

C(20A)-C(15A)-P(1)	119.8(2)	C(25B)-C(26B)-C(21B)	120.0
C(17A)-C(16A)-C(15A)	120.0	F(1)-C(41)-F(3)	108.1(2)
C(18A)-C(17A)-C(16A)	120.0	F(1)-C(41)-F(2)	107.5(2)
C(17A)-C(18A)-C(19A)	120.0	F(3)-C(41)-F(2)	106.5(2)
C(20A)-C(19A)-C(18A)	120.0	F(1)-C(41)-S(1)	112.54(16)
C(19A)-C(20A)-C(15A)	120.0	F(3)-C(41)-S(1)	110.47(18)
C(16B)-C(15B)-C(20B)	120.0	F(2)-C(41)-S(1)	111.57(17)
C(16B)-C(15B)-P(1)	123.87(19)	O(8)-S(1)-O(7)	114.72(10)
C(20B)-C(15B)-P(1)	116.11(19)	O(8)-S(1)-O(6)	115.22(9)
C(17B)-C(16B)-C(15B)	120.0	O(7)-S(1)-O(6)	115.03(9)
C(18B)-C(17B)-C(16B)	120.0	O(8)-S(1)-C(41)	103.43(10)
C(17B)-C(18B)-C(19B)	120.0	O(7)-S(1)-C(41)	103.18(11)
C(20B)-C(19B)-C(18B)	120.0	O(6)-S(1)-C(41)	102.82(10)
C(19B)-C(20B)-C(15B)	120.0		
C(22A)-C(21A)-C(26A)	120.0		
C(22A)-C(21A)-P(1)	114.2(2)		
C(26A)-C(21A)-P(1)	125.8(2)		
C(21A)-C(22A)-C(23A)	120.0		
C(24A)-C(23A)-C(22A)	120.0		
C(23A)-C(24A)-C(25A)	120.0		
C(26A)-C(25A)-C(24A)	120.0		
C(25A)-C(26A)-C(21A)	120.0		
C(22B)-C(21B)-C(26B)	120.0		
C(22B)-C(21B)-P(1)	122.42(13)		
C(26B)-C(21B)-P(1)	117.40(13)		
C(23B)-C(22B)-C(21B)	120.0		
C(22B)-C(23B)-C(24B)	120.0		
C(23B)-C(24B)-C(25B)	120.0		
C(26B)-C(25B)-C(24B)	120.0		

Table 5. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for [1-M_1][OTf] (AJMM45) (CCDC 779779). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Re(1)	139(1)	241(1)	142(1)	-25(1)	-12(1)	-9(1)
P(1)	154(2)	288(3)	193(2)	12(2)	-52(2)	8(2)
O(1)	225(7)	313(8)	341(8)	72(6)	1(6)	-12(6)
O(2)	359(9)	1035(16)	246(9)	-252(10)	-38(7)	19(10)
O(3)	348(9)	408(9)	347(9)	-66(7)	30(7)	-165(7)
O(4)	270(7)	302(7)	196(7)	-60(6)	-53(6)	11(6)
O(5)	290(8)	285(8)	363(9)	-28(7)	24(7)	71(6)
B(1)	197(10)	228(11)	348(13)	25(9)	-25(9)	4(8)
C(1)	179(9)	294(10)	208(9)	6(8)	-34(7)	47(7)
C(2)	203(10)	543(14)	240(10)	-80(10)	-9(8)	1(9)
C(3)	222(9)	323(11)	211(9)	-90(8)	-15(7)	-26(8)
C(4)	146(8)	195(8)	220(9)	-25(7)	-13(7)	17(6)
C(5)	234(9)	231(9)	218(9)	-46(7)	33(7)	-41(8)
C(6)	149(8)	222(9)	277(10)	-22(7)	-53(7)	-6(7)
C(7)	291(12)	393(13)	583(16)	-126(12)	-180(12)	124(10)
C(8)	230(12)	548(18)	1210(30)	-407(19)	69(15)	-107(12)
C(9)	485(16)	393(15)	850(20)	-222(15)	319(15)	-122(13)
C(10)	578(17)	271(12)	576(17)	-107(12)	-82(14)	-27(12)
C(11)	235(11)	292(12)	693(18)	-133(12)	-68(11)	34(9)
C(12)	720(20)	301(14)	950(30)	-47(15)	233(19)	-133(15)
C(13)	1170(40)	416(19)	1120(30)	270(20)	-230(30)	180(20)
C(14)	1090(30)	650(20)	680(20)	39(18)	-330(20)	510(20)
C(15A)	100(30)	260(30)	170(30)	100(20)	10(20)	50(20)
C(16A)	250(30)	190(20)	260(30)	0(20)	-50(20)	30(20)

C(17A)	400(40)	340(30)	210(30)	60(20)	20(20)	100(30)
C(18A)	370(40)	320(30)	510(40)	180(30)	20(30)	0(30)
C(19A)	670(80)	320(50)	510(70)	170(50)	-210(60)	-110(50)
C(20A)	230(30)	150(30)	280(40)	-60(30)	50(30)	90(20)
C(15B)	140(20)	720(30)	400(20)	300(20)	0(16)	-20(20)
C(16B)	370(30)	1760(60)	530(30)	730(30)	-150(20)	-250(30)
C(17B)	580(40)	2610(100)	1170(50)	1530(60)	-380(40)	-490(50)
C(18B)	580(40)	2900(120)	2190(90)	2340(90)	-430(50)	-570(60)
C(19B)	290(30)	1420(70)	1450(90)	1120(60)	-70(40)	-150(40)
C(20B)	200(20)	600(40)	800(40)	450(30)	-30(20)	10(30)
C(21A)	110(20)	110(20)	170(30)	30(20)	-15(19)	30(17)
C(22A)	190(30)	240(30)	220(30)	-70(20)	-50(20)	10(20)
C(23A)	190(30)	300(40)	410(40)	-120(30)	150(30)	-40(30)
C(24A)	230(30)	410(40)	380(40)	-120(30)	-30(30)	-150(30)
C(25A)	230(30)	530(40)	420(40)	-190(30)	-120(30)	-20(30)
C(26A)	230(30)	390(30)	250(30)	-40(20)	-80(20)	0(20)
C(21B)	167(17)	360(20)	165(16)	-28(17)	-68(13)	4(14)
C(22B)	181(16)	290(20)	211(16)	-51(14)	-8(13)	-7(14)
C(23B)	124(16)	430(30)	350(20)	-137(18)	22(15)	-39(16)
C(24B)	280(20)	840(40)	660(30)	-430(30)	-70(20)	-160(20)
C(25B)	290(20)	1450(50)	560(30)	-670(30)	-46(19)	-200(30)
C(26B)	186(16)	1260(40)	310(20)	-370(20)	-5(14)	-110(20)
C(41)	295(12)	442(14)	383(13)	124(11)	11(10)	40(10)
F(1)	470(9)	276(7)	919(13)	88(8)	-13(9)	-117(7)
F(2)	354(9)	505(10)	964(14)	242(9)	5(9)	146(7)
F(3)	1000(15)	743(12)	386(9)	290(8)	50(9)	145(11)
O(6)	184(7)	315(8)	381(9)	-6(7)	32(6)	-2(6)
O(7)	276(8)	439(10)	557(11)	-140(8)	-73(8)	-108(7)

O(8)	465(10)	298(8)	275(8)	14(6)	66(7)	13(7)
S(1)	194(2)	221(2)	263(2)	2(2)	9(2)	-37(2)

Table 1. Crystal data and structure refinement for 8 (AJMM42) (CCDC 768183).

Empirical formula	$C_{96}H_{112}B_4O_{10}P_4Re_2 \bullet 0.42(C_5H_{12}) \bullet 2.58(C_6H_6)$
Formula weight	2197.16
Crystallization Solvent	Benzene/pentane/heptane
Crystal Habit	Fragment
Crystal size	0.21 x 0.15 x 0.11 mm^3
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 9998 reflections used in lattice determination	2.40 to 29.21°	
Unit cell dimensions	a = 15.2592(6) Å	
	b = 27.8836(12) Å	β= 98.936(2)°
	c = 25.0134(11) Å	
Volume	10513.6(8) $Å^3$	
Z	4	
Crystal system	Monoclinic	
Space group	P $2_1/n$	
Density (calculated)	1.388 Mg/m^3	
F(000)	4496	
θ range for data collection	1.47 to 29.89°	
Completeness to θ = 29.89°	90.2 %	

Index ranges	$-20 \leq h \leq 21, -38 \leq k \leq 33, -35 \leq l \leq 33$
Data collection scan type	ω scans; 17 settings
Reflections collected	178438
Independent reflections	27378 [R_{int}= 0.0376]
Absorption coefficient	2.419 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7460 and 0.6254

Table 1 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	27378 / 0 / 1186
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	2.100
Final R indices [I>2σ(I), 22663 reflections]	R1 = 0.0332, *w*R2 = 0.0504
R indices (all data)	R1 = 0.0463, *w*R2 = 0.0510
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.005
Average shift/error	0.000
Largest diff. peak and hole	1.707 and -1.341 e.Å^{-3}

Special Refinement Details

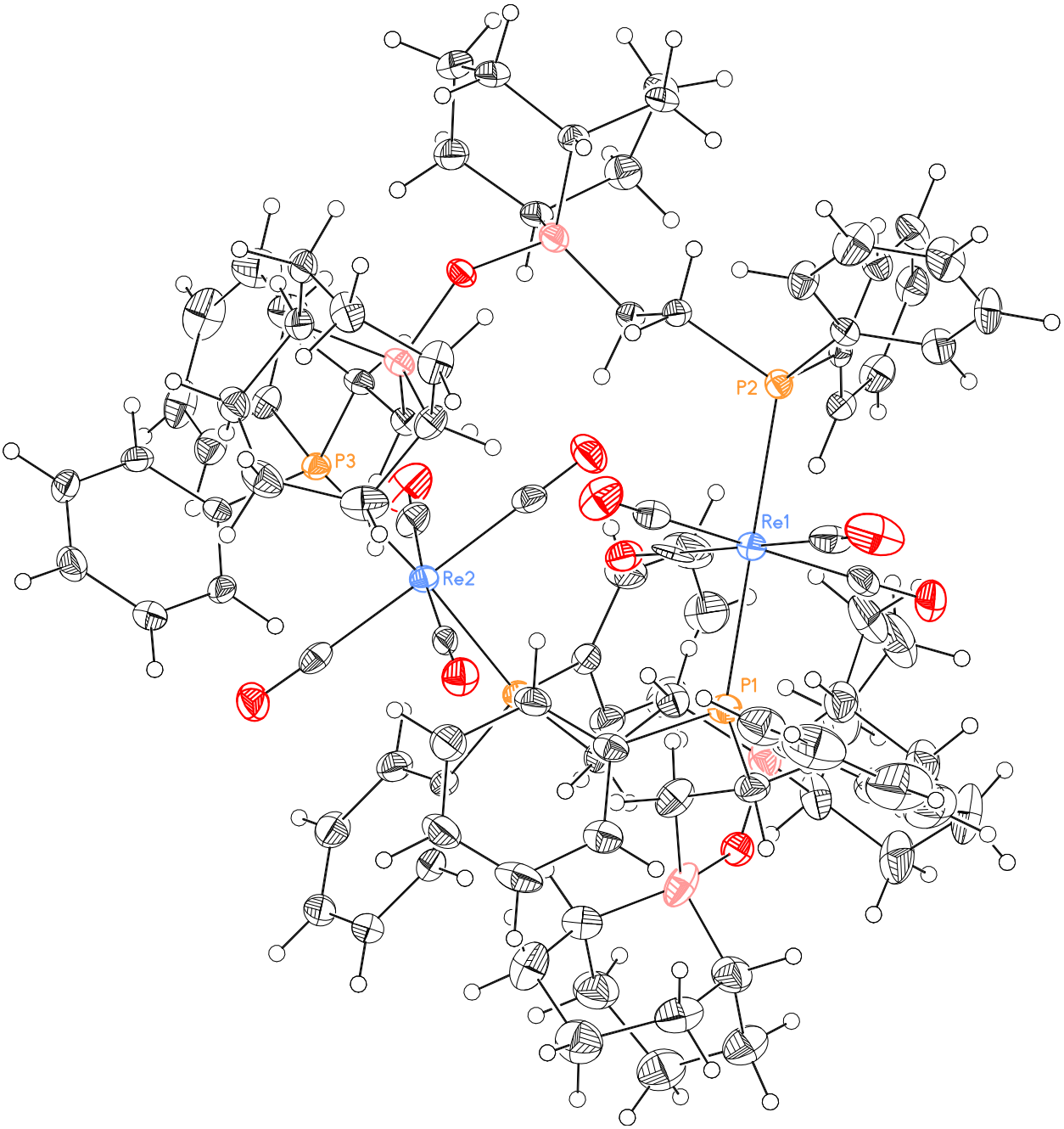
Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

There are three sites containing solvent, two contain benzene only. The third site is a mixture of benzene and pentane. The benzene in this site was restrained to an ideal hexagon and the pentane had no restraints applied.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will

be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.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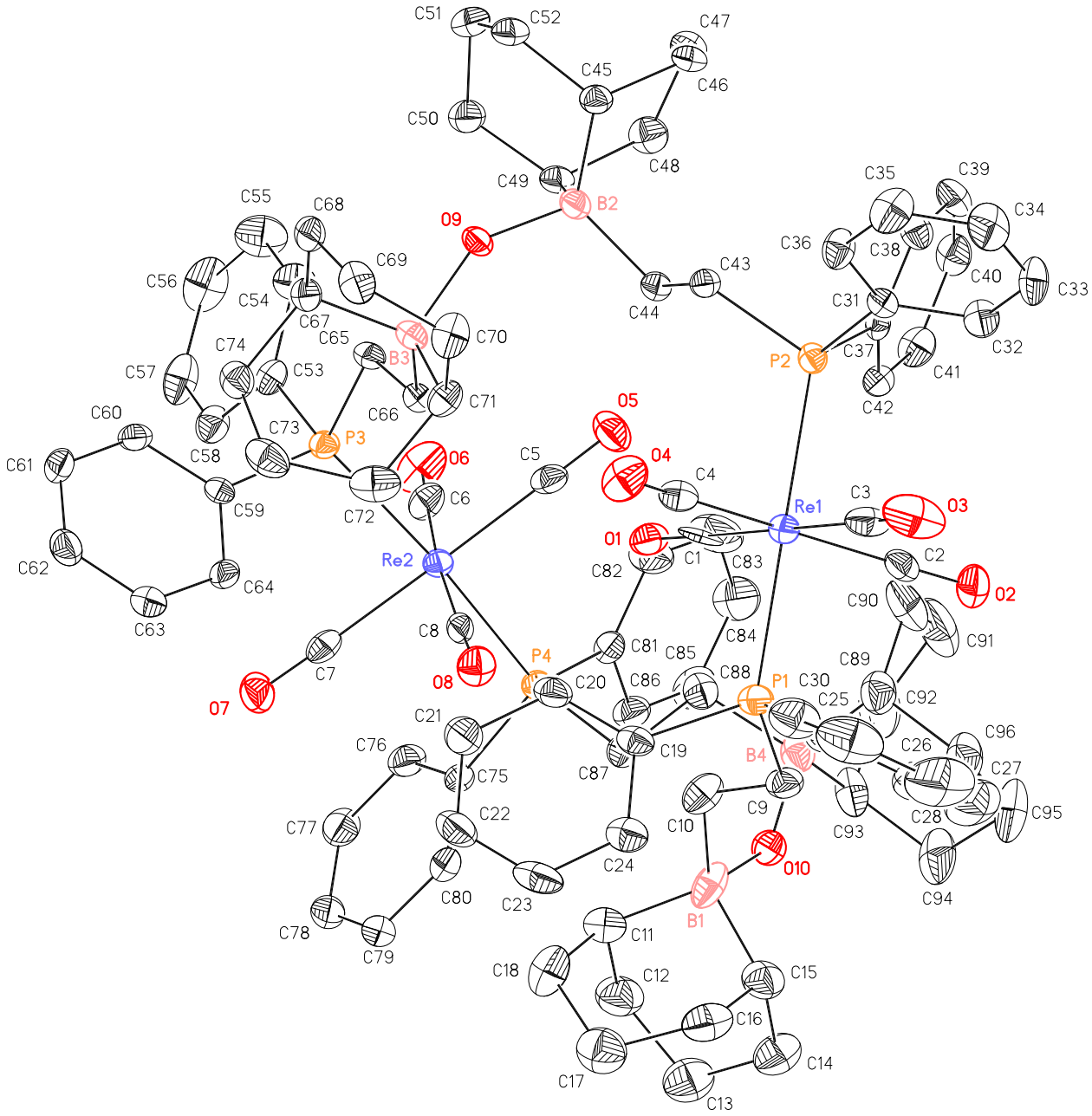
P3
Re1
Re2
P1


C51
C52
C47
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C48
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B2
09
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C67
C65
B3
C70
C74
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C53
C66
C71
C60
C73
P3
06
C61
C58
C5
05
04
C4
C59
C72
C6
Re1
C3
03
01
C1
C83
C2
02
C62
Re2
C82
C90
C64
C63
C8
C84
C91
C81
C85
C89
P4
C7
08
C20
C86
C88
P1
C30
C25
C92
07
C21
C96
C76
C19
B4
C26
C27
C75
C87
C9
C28
C95
C77
C22
C10
C93
C24
010
C80
C23
B1
C94
C78
C11
C79
C18
C12
C15
C16
C14
C17
C13
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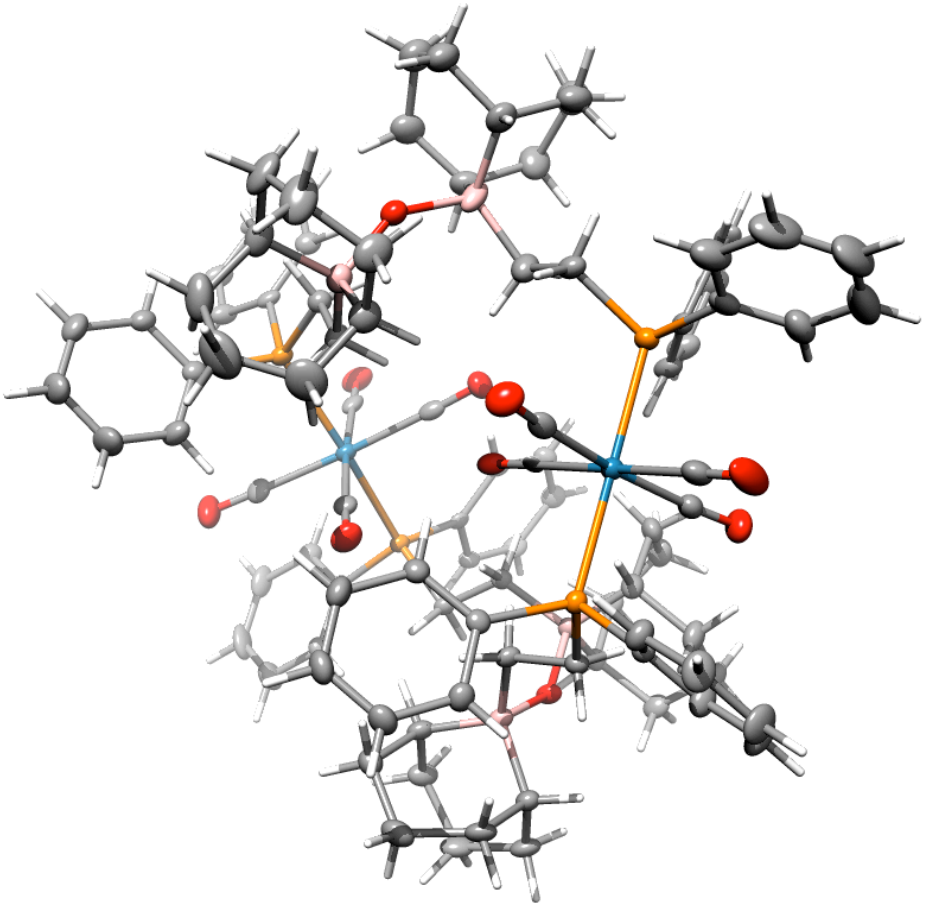
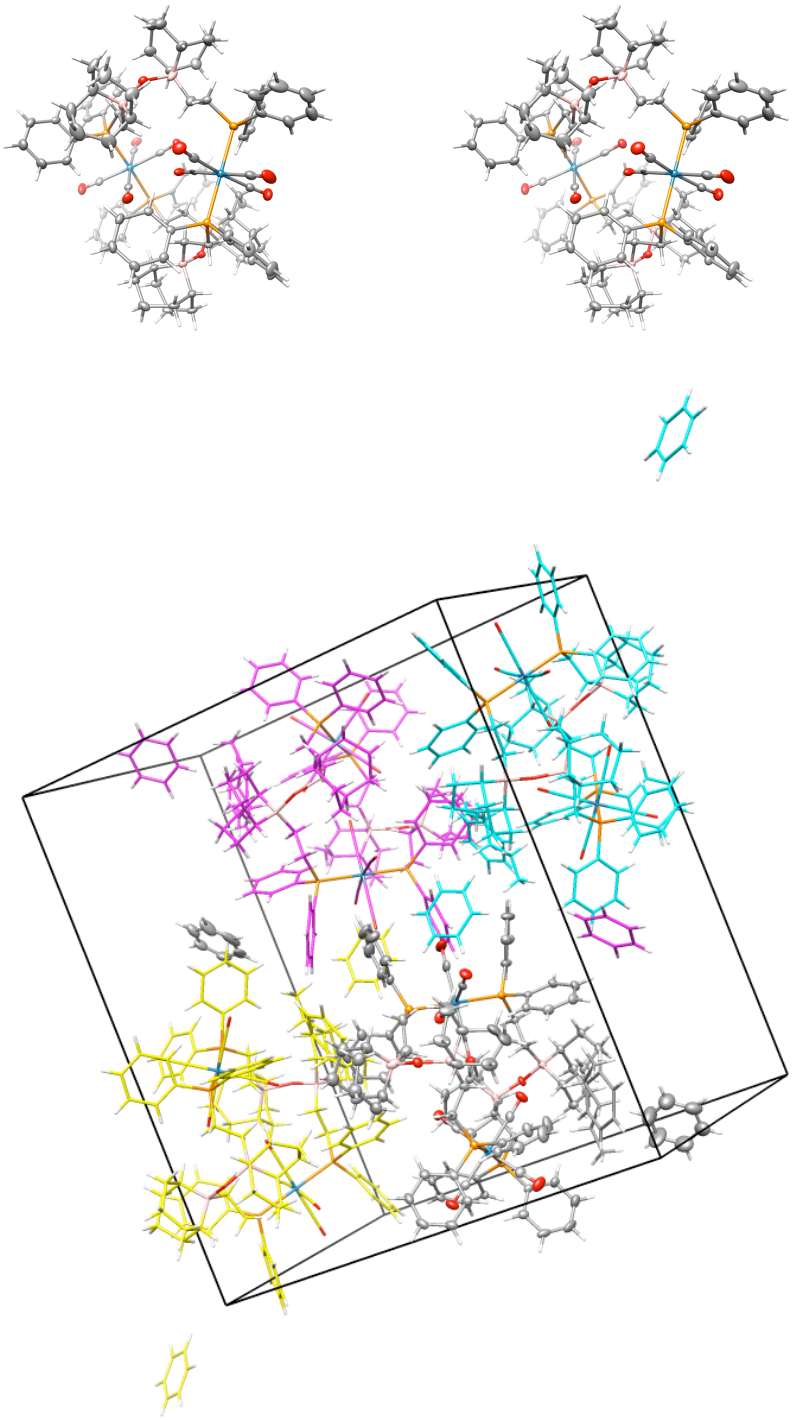
P2
C42
C44
C43





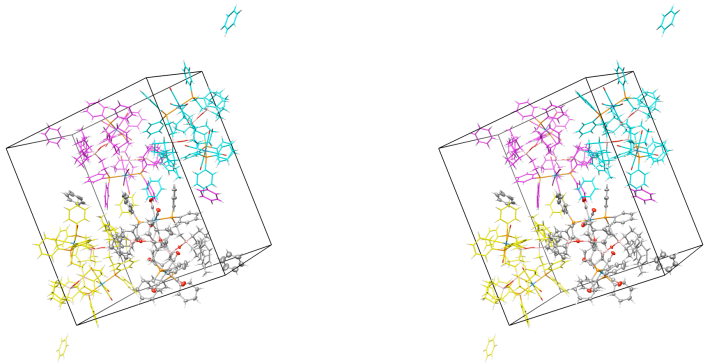


Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 8 (AJMM42) (CCDC 768183). U(eq) is defined at he trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
Re(1)	3351(1)	6419(1)	3945(1)	18(1)	1
Re(2)	1546(1)	9026(1)	3821(1)	18(1)	1
P(1)	2306(1)	6227(1)	4561(1)	22(1)	1
P(2)	4392(1)	6613(1)	3323(1)	17(1)	1
P(3)	2982(1)	9387(1)	4179(1)	17(1)	1
P(4)	35(1)	8764(1)	3472(1)	19(1)	1
O(1)	2618(1)	7471(1)	3852(1)	27(1)	1
O(2)	1979(1)	5996(1)	3004(1)	36(1)	1
O(3)	4127(2)	5380(1)	4058(1)	53(1)	1
O(4)	4834(1)	6591(1)	4936(1)	38(1)	1
O(5)	2442(1)	8370(1)	3043(1)	34(1)	1
O(6)	1234(1)	9841(1)	2955(1)	43(1)	1
O(7)	768(1)	9657(1)	4675(1)	34(1)	1
O(8)	1735(1)	8140(1)	4603(1)	29(1)	1
O(9)	5530(1)	8237(1)	4024(1)	21(1)	1
O(10)	-578(1)	7075(1)	3694(1)	25(1)	1
B(1)	-251(2)	6957(1)	4324(1)	32(1)	1
B(2)	5355(2)	8071(1)	3406(1)	21(1)	1
B(3)	5026(2)	8335(1)	4530(1)	18(1)	1
B(4)	-247(2)	7267(1)	3158(1)	26(1)	1
C(1)	2868(2)	7081(1)	3875(1)	21(1)	1
C(2)	2462(2)	6173(1)	3340(1)	23(1)	1
C(3)	3836(2)	5755(1)	4014(1)	32(1)	1
C(4)	4286(2)	6560(1)	4572(1)	25(1)	1

C(5)	2110(2)	8611(1)	3318(1)	24(1)	1
C(6)	1354(2)	9549(1)	3272(1)	27(1)	1
C(7)	1039(2)	9426(1)	4362(1)	23(1)	1
C(8)	1682(2)	8468(1)	4329(1)	22(1)	1
C(9)	1124(2)	6332(1)	4312(1)	26(1)	1
C(10)	821(2)	6857(1)	4386(1)	32(1)	1
C(11)	-506(2)	7402(1)	4694(1)	36(1)	1
C(12)	-1501(2)	7532(1)	4516(1)	41(1)	1
C(13)	-2151(2)	7112(1)	4532(1)	45(1)	1
C(14)	-1849(2)	6638(1)	4332(1)	41(1)	1
C(15)	-852(2)	6522(1)	4487(1)	34(1)	1
C(16)	-604(2)	6407(1)	5091(1)	42(1)	1
C(17)	-695(2)	6825(1)	5487(1)	46(1)	1
C(18)	-293(2)	7291(1)	5299(1)	42(1)	1
C(19)	2415(2)	6521(1)	5216(1)	22(1)	1
C(20)	2811(2)	6963(1)	5322(1)	27(1)	1
C(21)	2725(2)	7211(1)	5793(1)	36(1)	1
C(22)	2228(2)	7021(1)	6156(1)	37(1)	1
C(23)	1836(2)	6581(1)	6056(1)	36(1)	1
C(24)	1932(2)	6325(1)	5598(1)	29(1)	1
C(25)	2413(2)	5596(1)	4742(1)	29(1)	1
C(26)	1850(2)	5254(1)	4466(1)	43(1)	1
C(27)	1991(3)	4771(1)	4583(2)	62(1)	1
C(28)	2685(3)	4629(1)	4970(2)	68(1)	1
C(29)	3245(3)	4966(1)	5251(1)	59(1)	1
C(30)	3105(2)	5448(1)	5131(1)	40(1)	1
C(31)	5154(2)	6118(1)	3261(1)	18(1)	1
C(32)	4868(2)	5716(1)	2951(1)	26(1)	1
C(33)	5433(2)	5328(1)	2928(1)	32(1)	1

C(34)	6283(2)	5342(1)	3204(1)	36(1)	1
C(35)	6571(2)	5735(1)	3508(1)	36(1)	1
C(36)	6011(2)	6121(1)	3539(1)	26(1)	1
C(37)	3940(2)	6757(1)	2623(1)	17(1)	1
C(38)	4509(2)	6746(1)	2235(1)	23(1)	1
C(39)	4234(2)	6919(1)	1719(1)	28(1)	1
C(40)	3396(2)	7106(1)	1578(1)	28(1)	1
C(41)	2820(2)	7115(1)	1956(1)	28(1)	1
C(42)	3099(2)	6944(1)	2476(1)	21(1)	1
C(43)	5113(2)	7129(1)	3512(1)	19(1)	1
C(44)	4678(2)	7618(1)	3362(1)	20(1)	1
C(45)	6330(2)	7968(1)	3242(1)	21(1)	1
C(46)	6211(2)	7810(1)	2646(1)	26(1)	1
C(47)	5720(2)	8169(1)	2249(1)	32(1)	1
C(48)	4889(2)	8380(1)	2423(1)	28(1)	1
C(49)	4982(2)	8525(1)	3026(1)	23(1)	1
C(50)	5575(2)	8966(1)	3173(1)	28(1)	1
C(51)	6558(2)	8886(1)	3130(1)	32(1)	1
C(52)	6937(2)	8406(1)	3356(1)	28(1)	1
C(53)	3067(2)	9976(1)	3872(1)	20(1)	1
C(54)	3631(2)	10061(1)	3496(1)	28(1)	1
C(55)	3607(2)	10497(1)	3228(1)	41(1)	1
C(56)	3026(2)	10849(1)	3328(1)	41(1)	1
C(57)	2467(2)	10776(1)	3704(1)	32(1)	1
C(58)	2499(2)	10344(1)	3977(1)	26(1)	1
C(59)	3198(2)	9512(1)	4904(1)	17(1)	1
C(60)	3782(2)	9876(1)	5104(1)	21(1)	1
C(61)	4029(2)	9939(1)	5653(1)	25(1)	1
C(62)	3706(2)	9638(1)	6018(1)	27(1)	1

C(63)	3117(2)	9282(1)	5828(1)	25(1)	1
C(64)	2859(2)	9220(1)	5275(1)	21(1)	1
C(65)	3979(2)	9061(1)	4085(1)	19(1)	1
C(66)	4042(2)	8552(1)	4317(1)	18(1)	1
C(67)	5689(2)	8682(1)	4923(1)	20(1)	1
C(68)	6612(2)	8449(1)	5084(1)	25(1)	1
C(69)	6605(2)	7945(1)	5321(1)	29(1)	1
C(70)	5897(2)	7615(1)	5015(1)	30(1)	1
C(71)	4974(2)	7845(1)	4875(1)	24(1)	1
C(72)	4563(2)	7957(1)	5388(1)	34(1)	1
C(73)	4978(2)	8381(1)	5732(1)	34(1)	1
C(74)	5250(2)	8808(1)	5417(1)	26(1)	1
C(75)	-745(2)	9096(1)	3815(1)	20(1)	1
C(76)	-939(2)	9570(1)	3684(1)	27(1)	1
C(77)	-1470(2)	9839(1)	3972(1)	32(1)	1
C(78)	-1807(2)	9631(1)	4396(1)	32(1)	1
C(79)	-1629(2)	9166(1)	4531(1)	30(1)	1
C(80)	-1098(2)	8890(1)	4242(1)	25(1)	1
C(81)	-370(2)	8867(1)	2757(1)	21(1)	1
C(82)	193(2)	8834(1)	2367(1)	34(1)	1
C(83)	-151(2)	8851(1)	1821(1)	49(1)	1
C(84)	-1041(2)	8921(1)	1657(1)	43(1)	1
C(85)	-1600(2)	8966(1)	2034(1)	35(1)	1
C(86)	-1268(2)	8935(1)	2579(1)	26(1)	1
C(87)	-246(2)	8140(1)	3558(1)	23(1)	1
C(88)	288(2)	7771(1)	3293(1)	24(1)	1
C(89)	332(2)	6858(1)	2912(1)	32(1)	1
C(90)	600(2)	7049(1)	2387(1)	48(1)	1
C(91)	-165(2)	7237(1)	1969(1)	58(1)	1

C(92)	-899(2)	7522(1)	2196(1)	50(1)	1
C(93)	-1144(2)	7323(1)	2721(1)	34(1)	1
C(94)	-1661(2)	6851(1)	2642(1)	44(1)	1
C(95)	-1115(2)	6417(1)	2495(1)	51(1)	1
C(96)	-186(2)	6381(1)	2836(1)	40(1)	1
C(1A)	4461(4)	4097(1)	8574(2)	79(2)	1
C(2A)	4850(3)	4023(1)	9124(2)	68(1)	1
C(3A)	4537(2)	3656(1)	9404(1)	47(1)	1
C(4A)	3877(2)	3369(1)	9159(1)	50(1)	1
C(5A)	3503(2)	3437(2)	8637(2)	67(1)	1
C(6A)	3777(3)	3795(2)	8348(2)	76(2)	1
C(1B)	5504(4)	9619(2)	1710(2)	112(2)	1
C(2B)	5879(4)	10047(2)	1840(2)	118(2)	1
C(3B)	6038(3)	10324(2)	1417(2)	85(1)	1
C(4B)	5860(3)	10161(2)	878(2)	70(1)	1
C(5B)	5489(3)	9742(2)	774(2)	70(1)	1
C(6B)	5311(3)	9460(2)	1188(2)	80(1)	1
C(1D)	2608(3)	9009(2)	1920(2)	80(2)	0.576(4)
C(2D)	2073(3)	9345(2)	1616(2)	91(3)	0.576(4)
C(3D)	1598(3)	9217(2)	1116(2)	77(2)	0.576(4)
C(4D)	1659(3)	8754(2)	921(2)	84(3)	0.576(4)
C(5D)	2195(4)	8418(2)	1226(3)	122(4)	0.576(4)
C(6D)	2670(4)	8545(2)	1725(3)	224(9)	0.576(4)
C(1E)	2819(7)	9773(4)	2014(4)	100(4)	0.424(4)
C(2E)	2863(9)	9309(5)	2064(5)	134(5)	0.424(4)

C(3E)	2415(7)	8966(3)	1574(4)	72(3)	0.424(4)
C(4E)	2387(8)	8491(3)	1677(3)	63(3)	0.424(4)
C(5E)	1818(7)	8244(4)	1151(4)	78(3)	0.424(4)

Table 3. Selected bond lengths [Å] and angles [°] for 8 (AJMM42) (CCDC 768183).

Re(1)-C(1)	1.983(3)	C(1)-Re(1)-C(4)	95.62(11)
Re(1)-C(4)	1.989(3)	C(1)-Re(1)-C(2)	93.09(11)
Re(1)-C(2)	1.991(3)	C(4)-Re(1)-C(2)	171.12(11)
Re(1)-C(3)	1.992(3)	C(1)-Re(1)-C(3)	179.94(16)
Re(1)-P(1)	2.4437(6)	C(4)-Re(1)-C(3)	84.43(12)
Re(1)-P(2)	2.4490(6)	C(2)-Re(1)-C(3)	86.86(11)
Re(2)-C(6)	1.995(3)	C(1)-Re(1)-P(1)	89.41(6)
Re(2)-C(8)	1.998(3)	C(4)-Re(1)-P(1)	90.19(7)
Re(2)-C(5)	1.999(3)	C(2)-Re(1)-P(1)	88.16(7)
Re(2)-C(7)	1.999(3)	C(3)-Re(1)-P(1)	90.56(7)
Re(2)-P(4)	2.4475(7)	C(1)-Re(1)-P(2)	90.47(6)
Re(2)-P(3)	2.4496(7)	C(4)-Re(1)-P(2)	90.09(7)
		C(2)-Re(1)-P(2)	91.58(7)
		C(3)-Re(1)-P(2)	89.56(7)
		P(1)-Re(1)-P(2)	179.70(2)
		C(6)-Re(2)-C(8)	175.49(10)
		C(6)-Re(2)-C(5)	91.18(10)
		C(8)-Re(2)-C(5)	86.44(10)
		C(6)-Re(2)-C(7)	91.53(10)
		C(8)-Re(2)-C(7)	91.00(10)
		C(5)-Re(2)-C(7)	176.48(10)
		C(6)-Re(2)-P(4)	86.72(8)
		C(8)-Re(2)-P(4)	89.64(7)
		C(5)-Re(2)-P(4)	94.33(7)
		C(7)-Re(2)-P(4)	88.06(7)
		C(6)-Re(2)-P(3)	88.77(8)
		C(8)-Re(2)-P(3)	95.09(7)

C(5)-Re(2)-P(3)	91.14(7)	P(4)-Re(2)-P(3)	172.98(2)
C(7)-Re(2)-P(3)	86.67(7)		

Table 4. Bond lengths [Å] and angles [°] for 8 (AJMM42) (CCDC 768183).

Re(1)-C(1)	1.983(3)	O(4)-C(4)	1.140(3)
Re(1)-C(4)	1.989(3)	O(5)-C(5)	1.138(3)
Re(1)-C(2)	1.991(3)	O(6)-C(6)	1.131(3)
Re(1)-C(3)	1.992(3)	O(7)-C(7)	1.141(3)
Re(1)-P(1)	2.4437(6)	O(8)-C(8)	1.138(3)
Re(1)-P(2)	2.4490(6)	O(9)-B(2)	1.597(3)
Re(2)-C(6)	1.995(3)	O(9)-B(3)	1.603(3)
Re(2)-C(8)	1.998(3)	O(10)-B(4)	1.599(3)
Re(2)-C(5)	1.999(3)	O(10)-B(1)	1.609(4)
Re(2)-C(7)	1.999(3)	B(1)-C(15)	1.610(4)
Re(2)-P(4)	2.4475(7)	B(1)-C(11)	1.632(4)
Re(2)-P(3)	2.4496(7)	B(1)-C(10)	1.643(4)
P(1)-C(25)	1.816(3)	B(2)-C(44)	1.626(4)
P(1)-C(19)	1.818(3)	B(2)-C(45)	1.629(3)
P(1)-C(9)	1.838(2)	B(2)-C(49)	1.632(4)
P(2)-C(37)	1.825(2)	B(3)-C(67)	1.618(4)
P(2)-C(31)	1.827(2)	B(3)-C(71)	1.624(4)
P(2)-C(43)	1.827(2)	B(3)-C(66)	1.629(4)
P(3)-C(65)	1.819(2)	B(4)-C(89)	1.620(4)
P(3)-C(59)	1.827(2)	B(4)-C(93)	1.621(4)
P(3)-C(53)	1.827(3)	B(4)-C(88)	1.634(4)
P(4)-C(87)	1.812(2)	C(9)-C(10)	1.556(3)
P(4)-C(81)	1.822(3)	C(11)-C(18)	1.529(4)
P(4)-C(75)	1.824(2)	C(11)-C(12)	1.557(4)
O(1)-C(1)	1.151(3)	C(12)-C(13)	1.539(4)
O(2)-C(2)	1.140(3)	C(13)-C(14)	1.510(4)
O(3)-C(3)	1.134(3)	C(14)-C(15)	1.546(4)

C(15)-C(16)	1.534(4)	C(45)-C(46)	1.538(3)
C(16)-C(17)	1.548(4)	C(46)-C(47)	1.524(3)
C(17)-C(18)	1.540(4)	C(47)-C(48)	1.523(3)
C(19)-C(20)	1.380(3)	C(48)-C(49)	1.545(3)
C(19)-C(24)	1.404(3)	C(49)-C(50)	1.538(3)
C(20)-C(21)	1.389(3)	C(50)-C(51)	1.537(3)
C(21)-C(22)	1.377(3)	C(51)-C(52)	1.531(4)
C(22)-C(23)	1.371(4)	C(53)-C(54)	1.389(3)
C(23)-C(24)	1.377(3)	C(53)-C(58)	1.396(3)
C(25)-C(30)	1.384(4)	C(54)-C(55)	1.385(3)
C(25)-C(26)	1.394(4)	C(55)-C(56)	1.371(4)
C(26)-C(27)	1.387(4)	C(56)-C(57)	1.381(4)
C(27)-C(28)	1.376(5)	C(57)-C(58)	1.380(3)
C(28)-C(29)	1.386(5)	C(59)-C(60)	1.391(3)
C(29)-C(30)	1.384(4)	C(59)-C(64)	1.393(3)
C(31)-C(36)	1.383(3)	C(60)-C(61)	1.379(3)
C(31)-C(32)	1.393(3)	C(61)-C(62)	1.386(3)
C(32)-C(33)	1.389(3)	C(62)-C(63)	1.375(3)
C(33)-C(34)	1.373(4)	C(63)-C(64)	1.388(3)
C(34)-C(35)	1.367(4)	C(65)-C(66)	1.532(3)
C(35)-C(36)	1.383(3)	C(67)-C(74)	1.535(3)
C(37)-C(42)	1.380(3)	C(67)-C(68)	1.546(3)
C(37)-C(38)	1.400(3)	C(68)-C(69)	1.526(3)
C(38)-C(39)	1.380(3)	C(69)-C(70)	1.532(3)
C(39)-C(40)	1.377(3)	C(70)-C(71)	1.537(3)
C(40)-C(41)	1.387(3)	C(71)-C(72)	1.547(3)
C(41)-C(42)	1.389(3)	C(72)-C(73)	1.539(4)
C(43)-C(44)	1.536(3)	C(73)-C(74)	1.520(3)
C(45)-C(52)	1.533(3)	C(75)-C(76)	1.384(3)

C(75)-C(80)	1.393(3)	C(3B)-C(4B)	1.406(5)
C(76)-C(77)	1.385(3)	C(4B)-C(5B)	1.307(5)
C(77)-C(78)	1.378(3)	C(5B)-C(6B)	1.361(5)
C(78)-C(79)	1.357(4)	C(1D)-C(2D)	1.3900
C(79)-C(80)	1.399(3)	C(1D)-C(6D)	1.3900
C(81)-C(86)	1.386(3)	C(2D)-C(3D)	1.3900
C(81)-C(82)	1.398(3)	C(3D)-C(4D)	1.3900
C(82)-C(83)	1.386(4)	C(4D)-C(5D)	1.3900
C(83)-C(84)	1.370(4)	C(5D)-C(6D)	1.3900
C(84)-C(85)	1.372(3)	C(1E)-C(2E)	1.301(14)
C(85)-C(86)	1.382(3)	C(2E)-C(3E)	1.620(16)
C(87)-C(88)	1.526(3)	C(3E)-C(4E)	1.350(11)
C(89)-C(90)	1.530(4)	C(4E)-C(5E)	1.615(13)
C(89)-C(96)	1.545(4)		
C(90)-C(91)	1.534(4)	C(1)-Re(1)-C(4)	95.62(11)
C(91)-C(92)	1.550(4)	C(1)-Re(1)-C(2)	93.09(11)
C(92)-C(93)	1.525(4)	C(4)-Re(1)-C(2)	171.12(11)
C(93)-C(94)	1.530(4)	C(1)-Re(1)-C(3)	179.94(16)
C(94)-C(95)	1.546(4)	C(4)-Re(1)-C(3)	84.43(12)
C(95)-C(96)	1.541(4)	C(2)-Re(1)-C(3)	86.86(11)
C(1A)-C(6A)	1.392(6)	C(1)-Re(1)-P(1)	89.41(6)
C(1A)-C(2A)	1.427(5)	C(4)-Re(1)-P(1)	90.19(7)
C(2A)-C(3A)	1.368(4)	C(2)-Re(1)-P(1)	88.16(7)
C(3A)-C(4A)	1.355(4)	C(3)-Re(1)-P(1)	90.56(7)
C(4A)-C(5A)	1.355(4)	C(1)-Re(1)-P(2)	90.47(6)
C(5A)-C(6A)	1.338(5)	C(4)-Re(1)-P(2)	90.09(7)
C(1B)-C(2B)	1.341(5)	C(2)-Re(1)-P(2)	91.58(7)
C(1B)-C(6B)	1.370(5)	C(3)-Re(1)-P(2)	89.56(7)
C(2B)-C(3B)	1.363(5)	P(1)-Re(1)-P(2)	179.70(2)

C(6)-Re(2)-C(8)	175.49(10)	C(59)-P(3)-C(53)	103.38(11)
C(6)-Re(2)-C(5)	91.18(10)	C(65)-P(3)-Re(2)	117.84(8)
C(8)-Re(2)-C(5)	86.44(10)	C(59)-P(3)-Re(2)	117.03(8)
C(6)-Re(2)-C(7)	91.53(10)	C(53)-P(3)-Re(2)	109.52(8)
C(8)-Re(2)-C(7)	91.00(10)	C(87)-P(4)-C(81)	102.64(12)
C(5)-Re(2)-C(7)	176.48(10)	C(87)-P(4)-C(75)	104.30(11)
C(6)-Re(2)-P(4)	86.72(8)	C(81)-P(4)-C(75)	103.53(12)
C(8)-Re(2)-P(4)	89.64(7)	C(87)-P(4)-Re(2)	118.15(9)
C(5)-Re(2)-P(4)	94.33(7)	C(81)-P(4)-Re(2)	117.45(8)
C(7)-Re(2)-P(4)	88.06(7)	C(75)-P(4)-Re(2)	109.11(8)
C(6)-Re(2)-P(3)	88.77(8)	B(2)-O(9)-B(3)	141.72(18)
C(8)-Re(2)-P(3)	95.09(7)	B(4)-O(10)-B(1)	143.0(2)
C(5)-Re(2)-P(3)	91.14(7)	O(10)-B(1)-C(15)	107.4(2)
C(7)-Re(2)-P(3)	86.67(7)	O(10)-B(1)-C(11)	109.6(2)
P(4)-Re(2)-P(3)	172.98(2)	C(15)-B(1)-C(11)	103.4(2)
C(25)-P(1)-C(19)	102.71(12)	O(10)-B(1)-C(10)	106.3(2)
C(25)-P(1)-C(9)	106.50(13)	C(15)-B(1)-C(10)	116.5(2)
C(19)-P(1)-C(9)	100.35(11)	C(11)-B(1)-C(10)	113.4(2)
C(25)-P(1)-Re(1)	109.19(8)	O(9)-B(2)-C(44)	107.38(19)
C(19)-P(1)-Re(1)	119.47(8)	O(9)-B(2)-C(45)	105.8(2)
C(9)-P(1)-Re(1)	117.02(8)	C(44)-B(2)-C(45)	116.2(2)
C(37)-P(2)-C(31)	103.56(11)	O(9)-B(2)-C(49)	109.3(2)
C(37)-P(2)-C(43)	101.40(11)	C(44)-B(2)-C(49)	113.8(2)
C(31)-P(2)-C(43)	104.60(11)	C(45)-B(2)-C(49)	103.9(2)
C(37)-P(2)-Re(1)	118.12(8)	O(9)-B(3)-C(67)	104.51(18)
C(31)-P(2)-Re(1)	111.80(8)	O(9)-B(3)-C(71)	110.1(2)
C(43)-P(2)-Re(1)	115.71(8)	C(67)-B(3)-C(71)	104.9(2)
C(65)-P(3)-C(59)	101.45(11)	O(9)-B(3)-C(66)	109.70(19)
C(65)-P(3)-C(53)	106.16(11)	C(67)-B(3)-C(66)	115.7(2)

C(71)-B(3)-C(66)	111.6(2)	C(20)-C(19)-C(24)	118.5(2)
O(10)-B(4)-C(89)	110.2(2)	C(20)-C(19)-P(1)	123.53(19)
O(10)-B(4)-C(93)	104.7(2)	C(24)-C(19)-P(1)	116.9(2)
C(89)-B(4)-C(93)	105.4(2)	C(19)-C(20)-C(21)	120.7(2)
O(10)-B(4)-C(88)	109.1(2)	C(22)-C(21)-C(20)	120.1(3)
C(89)-B(4)-C(88)	113.6(2)	C(23)-C(22)-C(21)	119.6(3)
C(93)-B(4)-C(88)	113.5(2)	C(22)-C(23)-C(24)	121.0(3)
O(1)-C(1)-Re(1)	176.9(3)	C(23)-C(24)-C(19)	120.0(3)
O(2)-C(2)-Re(1)	174.5(2)	C(30)-C(25)-C(26)	119.1(3)
O(3)-C(3)-Re(1)	178.7(3)	C(30)-C(25)-P(1)	119.6(2)
O(4)-C(4)-Re(1)	173.0(3)	C(26)-C(25)-P(1)	121.0(2)
O(5)-C(5)-Re(2)	178.3(2)	C(27)-C(26)-C(25)	119.8(3)
O(6)-C(6)-Re(2)	178.8(3)	C(28)-C(27)-C(26)	120.3(4)
O(7)-C(7)-Re(2)	178.5(2)	C(27)-C(28)-C(29)	120.5(4)
O(8)-C(8)-Re(2)	177.1(2)	C(30)-C(29)-C(28)	119.1(4)
C(10)-C(9)-P(1)	113.87(18)	C(25)-C(30)-C(29)	121.2(3)
C(9)-C(10)-B(1)	117.3(2)	C(36)-C(31)-C(32)	118.3(2)
C(18)-C(11)-C(12)	112.2(2)	C(36)-C(31)-P(2)	121.1(2)
C(18)-C(11)-B(1)	112.0(3)	C(32)-C(31)-P(2)	120.5(2)
C(12)-C(11)-B(1)	108.8(2)	C(33)-C(32)-C(31)	120.5(3)
C(13)-C(12)-C(11)	114.7(2)	C(34)-C(33)-C(32)	120.0(3)
C(14)-C(13)-C(12)	115.3(2)	C(35)-C(34)-C(33)	120.0(3)
C(13)-C(14)-C(15)	116.0(3)	C(34)-C(35)-C(36)	120.4(3)
C(16)-C(15)-C(14)	111.9(2)	C(31)-C(36)-C(35)	120.8(3)
C(16)-C(15)-B(1)	110.2(2)	C(42)-C(37)-C(38)	118.3(2)
C(14)-C(15)-B(1)	110.9(2)	C(42)-C(37)-P(2)	122.49(17)
C(15)-C(16)-C(17)	116.1(3)	C(38)-C(37)-P(2)	118.54(19)
C(18)-C(17)-C(16)	111.1(2)	C(39)-C(38)-C(37)	120.6(2)
C(11)-C(18)-C(17)	116.0(3)	C(40)-C(39)-C(38)	120.6(2)

C(39)-C(40)-C(41)	119.6(2)	C(60)-C(61)-C(62)	120.6(2)
C(40)-C(41)-C(42)	119.8(2)	C(63)-C(62)-C(61)	119.4(2)
C(37)-C(42)-C(41)	121.2(2)	C(62)-C(63)-C(64)	120.2(2)
C(44)-C(43)-P(2)	114.53(17)	C(63)-C(64)-C(59)	120.9(2)
C(43)-C(44)-B(2)	115.3(2)	C(66)-C(65)-P(3)	114.67(15)
C(52)-C(45)-C(46)	112.8(2)	C(65)-C(66)-B(3)	117.9(2)
C(52)-C(45)-B(2)	111.2(2)	C(74)-C(67)-C(68)	112.3(2)
C(46)-C(45)-B(2)	108.6(2)	C(74)-C(67)-B(3)	108.50(19)
C(47)-C(46)-C(45)	114.5(2)	C(68)-C(67)-B(3)	111.5(2)
C(48)-C(47)-C(46)	114.5(2)	C(69)-C(68)-C(67)	115.3(2)
C(47)-C(48)-C(49)	115.2(2)	C(68)-C(69)-C(70)	113.9(2)
C(50)-C(49)-C(48)	113.8(2)	C(69)-C(70)-C(71)	114.4(2)
C(50)-C(49)-B(2)	110.0(2)	C(70)-C(71)-C(72)	111.7(2)
C(48)-C(49)-B(2)	109.7(2)	C(70)-C(71)-B(3)	110.8(2)
C(51)-C(50)-C(49)	114.2(2)	C(72)-C(71)-B(3)	109.3(2)
C(52)-C(51)-C(50)	114.7(2)	C(73)-C(72)-C(71)	115.7(2)
C(51)-C(52)-C(45)	116.4(2)	C(74)-C(73)-C(72)	115.7(2)
C(54)-C(53)-C(58)	118.0(2)	C(73)-C(74)-C(67)	115.2(2)
C(54)-C(53)-P(3)	122.0(2)	C(76)-C(75)-C(80)	118.8(2)
C(58)-C(53)-P(3)	119.71(18)	C(76)-C(75)-P(4)	120.37(19)
C(55)-C(54)-C(53)	120.3(3)	C(80)-C(75)-P(4)	120.7(2)
C(56)-C(55)-C(54)	120.6(3)	C(75)-C(76)-C(77)	121.0(2)
C(55)-C(56)-C(57)	120.2(3)	C(78)-C(77)-C(76)	119.5(3)
C(58)-C(57)-C(56)	119.2(3)	C(79)-C(78)-C(77)	120.6(3)
C(57)-C(58)-C(53)	121.6(2)	C(78)-C(79)-C(80)	120.4(2)
C(60)-C(59)-C(64)	118.1(2)	C(75)-C(80)-C(79)	119.7(3)
C(60)-C(59)-P(3)	120.14(18)	C(86)-C(81)-C(82)	118.0(2)
C(64)-C(59)-P(3)	121.42(19)	C(86)-C(81)-P(4)	120.27(18)
C(61)-C(60)-C(59)	120.7(2)	C(82)-C(81)-P(4)	121.4(2)

C(83)-C(82)-C(81)	120.3(3)	C(4B)-C(5B)-C(6B)	119.8(4)
C(84)-C(83)-C(82)	120.4(3)	C(5B)-C(6B)-C(1B)	120.0(4)
C(83)-C(84)-C(85)	120.0(3)	C(2D)-C(1D)-C(6D)	120.0
C(84)-C(85)-C(86)	120.1(3)	C(1D)-C(2D)-C(3D)	120.0
C(85)-C(86)-C(81)	121.1(2)	C(4D)-C(3D)-C(2D)	120.0
C(88)-C(87)-P(4)	116.27(16)	C(3D)-C(4D)-C(5D)	120.0
C(87)-C(88)-B(4)	112.8(2)	C(6D)-C(5D)-C(4D)	120.0
C(90)-C(89)-C(96)	113.1(2)	C(5D)-C(6D)-C(1D)	120.0
C(90)-C(89)-B(4)	108.4(2)	C(1E)-C(2E)-C(3E)	120.5(12)
C(96)-C(89)-B(4)	110.8(2)	C(4E)-C(3E)-C(2E)	117.2(9)
C(89)-C(90)-C(91)	115.3(2)	C(3E)-C(4E)-C(5E)	106.9(8)
C(90)-C(91)-C(92)	116.3(2)		
C(93)-C(92)-C(91)	114.6(3)		
C(92)-C(93)-C(94)	113.1(2)		
C(92)-C(93)-B(4)	108.7(2)		
C(94)-C(93)-B(4)	111.7(2)		
C(93)-C(94)-C(95)	114.7(2)		
C(96)-C(95)-C(94)	113.7(2)		
C(95)-C(96)-C(89)	114.9(3)		
C(6A)-C(1A)-C(2A)	118.5(4)		
C(3A)-C(2A)-C(1A)	118.4(4)		
C(4A)-C(3A)-C(2A)	120.4(3)		
C(3A)-C(4A)-C(5A)	121.6(4)		
C(6A)-C(5A)-C(4A)	120.4(4)		
C(5A)-C(6A)-C(1A)	120.6(4)		
C(2B)-C(1B)-C(6B)	122.7(5)		
C(1B)-C(2B)-C(3B)	115.9(5)		
C(2B)-C(3B)-C(4B)	122.0(4)		
C(5B)-C(4B)-C(3B)	119.5(4)		

Table 5. Anisotropic displacement parameters ($Å^2 x 10^4$) for 8 (AJMM42) (CCDC 768183). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Re(1)	172(1)	195(1)	179(1)	6(1)	33(1)	4(1)
Re(2)	136(1)	204(1)	190(1)	-15(1)	26(1)	0(1)
P(1)	192(4)	263(4)	208(4)	19(3)	40(3)	-17(3)
P(2)	164(3)	184(4)	169(3)	-13(3)	16(3)	10(3)
P(3)	142(3)	181(4)	191(3)	-2(3)	31(3)	4(3)
P(4)	152(4)	227(4)	207(4)	-21(3)	32(3)	-5(3)
O(1)	218(10)	228(12)	375(11)	9(9)	96(9)	-12(9)
O(2)	341(12)	377(13)	344(12)	-140(10)	30(10)	-63(10)
O(3)	654(17)	303(14)	734(17)	216(12)	401(14)	202(12)
O(4)	325(12)	447(14)	322(12)	69(10)	-86(10)	-50(10)
O(5)	284(11)	432(13)	303(11)	-107(10)	69(9)	66(10)
O(6)	421(13)	400(14)	400(13)	145(11)	-120(10)	-80(11)
O(7)	243(11)	370(13)	394(12)	-155(10)	54(9)	15(9)
O(8)	341(12)	248(12)	280(11)	33(9)	41(9)	-4(10)
O(9)	180(9)	309(11)	158(9)	-56(8)	49(7)	-13(8)
O(10)	216(10)	297(12)	235(10)	-26(9)	14(8)	-18(9)
B(1)	229(18)	230(20)	450(20)	-21(17)	-90(16)	-19(15)
B(2)	172(16)	261(19)	195(15)	-44(14)	43(13)	0(14)
B(3)	171(16)	233(18)	157(15)	-4(13)	41(12)	30(14)
B(4)	242(18)	280(20)	241(17)	-35(15)	7(14)	26(15)
C(1)	169(14)	314(18)	196(14)	121(13)	154(11)	100(13)
C(2)	273(16)	211(16)	242(15)	-3(13)	111(13)	45(13)
C(3)	299(17)	350(20)	336(17)	73(15)	158(14)	-18(15)
C(4)	244(16)	280(18)	241(15)	52(13)	78(13)	10(13)

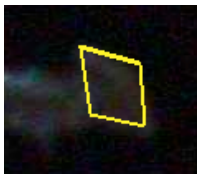
C(5)	165(14)	314(18)	227(14)	25(13)	13(11)	-55(13)
C(6)	213(15)	295(19)	274(16)	-5(14)	-28(12)	-42(13)
C(7)	136(14)	228(17)	304(16)	13(13)	-24(12)	-28(12)
C(8)	136(14)	302(19)	217(14)	-116(13)	21(11)	-29(12)
C(9)	179(14)	360(19)	241(14)	-5(13)	29(12)	-41(13)
C(10)	252(16)	311(19)	385(17)	25(15)	-30(13)	-39(14)
C(11)	321(18)	400(20)	375(18)	-19(15)	132(15)	-42(15)
C(12)	346(19)	430(20)	490(20)	5(17)	143(16)	42(16)
C(13)	323(19)	500(20)	530(20)	30(18)	50(16)	5(17)
C(14)	293(18)	420(20)	500(20)	29(17)	31(15)	-33(16)
C(15)	246(16)	390(20)	374(17)	-22(15)	65(14)	52(14)
C(16)	303(18)	430(20)	530(20)	70(18)	105(16)	-29(16)
C(17)	430(20)	530(20)	430(20)	32(18)	72(16)	25(18)
C(18)	460(20)	310(20)	460(20)	1(16)	-29(16)	-70(16)
C(19)	158(14)	321(18)	180(13)	27(12)	25(11)	34(13)
C(20)	179(15)	430(20)	218(14)	-28(14)	51(12)	-21(14)
C(21)	259(17)	490(20)	317(17)	-105(16)	39(14)	-48(15)
C(22)	266(17)	610(20)	236(16)	-104(16)	71(13)	-13(16)
C(23)	244(17)	620(20)	219(15)	73(16)	85(13)	44(16)
C(24)	230(15)	390(20)	248(15)	41(14)	31(12)	19(14)
C(25)	323(17)	275(18)	322(17)	61(14)	170(14)	-7(14)
C(26)	430(20)	300(20)	590(20)	32(17)	223(18)	-11(17)
C(27)	660(30)	340(20)	950(30)	20(20)	350(30)	-90(20)
C(28)	780(30)	350(30)	1010(40)	310(20)	420(30)	120(20)
C(29)	630(30)	620(30)	570(20)	290(20)	240(20)	180(20)
C(30)	460(20)	360(20)	405(19)	132(16)	158(16)	59(17)
C(31)	190(14)	186(16)	174(13)	10(11)	41(11)	22(12)
C(32)	218(15)	286(18)	275(15)	-19(13)	-2(12)	35(13)
C(33)	410(19)	191(17)	355(17)	-91(14)	-5(15)	24(14)

C(34)	354(19)	227(18)	490(20)	-17(15)	46(15)	152(15)
C(35)	219(16)	301(19)	520(20)	7(16)	-51(14)	67(14)
C(36)	257(16)	193(16)	320(16)	-24(13)	-14(13)	26(13)
C(37)	211(14)	122(15)	176(13)	-17(11)	20(11)	-18(11)
C(38)	236(15)	235(17)	217(14)	-16(12)	26(12)	44(12)
C(39)	352(17)	304(18)	198(14)	-20(13)	92(13)	32(14)
C(40)	344(17)	299(18)	178(14)	22(13)	-33(13)	-21(14)
C(41)	221(15)	282(18)	300(16)	16(13)	-43(13)	13(13)
C(42)	205(14)	213(16)	213(14)	-8(12)	34(12)	-28(12)
C(43)	173(14)	213(16)	185(13)	-5(11)	36(11)	-18(12)
C(44)	162(14)	215(16)	219(14)	-30(12)	48(11)	8(12)
C(45)	157(14)	258(17)	204(14)	-6(12)	36(11)	-5(12)
C(46)	202(15)	331(18)	269(15)	-52(13)	125(12)	-40(13)
C(47)	369(18)	390(20)	220(15)	-39(14)	113(13)	-88(15)
C(48)	288(16)	324(18)	234(15)	40(13)	27(12)	-5(14)
C(49)	154(14)	290(17)	259(14)	-31(13)	74(12)	-4(12)
C(50)	259(16)	238(17)	372(16)	-26(14)	120(13)	-18(13)
C(51)	251(16)	335(19)	418(18)	-60(15)	143(14)	-94(14)
C(52)	176(15)	359(18)	308(16)	-46(14)	99(12)	-34(13)
C(53)	179(14)	187(16)	218(14)	19(12)	-38(11)	-5(12)
C(54)	290(16)	275(18)	295(16)	84(14)	57(13)	41(14)
C(55)	450(20)	410(20)	369(18)	168(16)	108(16)	30(17)
C(56)	570(20)	270(20)	340(18)	145(15)	-96(16)	-14(17)
C(57)	350(18)	183(17)	387(18)	-7(14)	-104(14)	42(14)
C(58)	231(15)	240(17)	301(16)	-27(13)	2(12)	-2(13)
C(59)	122(13)	182(15)	205(13)	-15(11)	51(11)	38(11)
C(60)	172(14)	212(16)	250(14)	10(12)	74(12)	-17(12)
C(61)	211(15)	247(17)	286(15)	-75(13)	22(12)	-50(13)
C(62)	264(16)	343(19)	202(14)	-70(13)	31(12)	-2(14)

C(63)	246(15)	277(17)	233(15)	6(13)	84(12)	-8(13)
C(64)	150(14)	198(16)	270(15)	-43(12)	46(12)	-16(12)
C(65)	158(13)	224(16)	184(13)	-1(12)	53(11)	18(12)
C(66)	184(14)	179(15)	170(13)	-9(11)	38(11)	10(12)
C(67)	218(14)	196(16)	187(13)	0(11)	18(11)	8(12)
C(68)	201(15)	337(19)	204(14)	-75(13)	-7(11)	-30(13)
C(69)	238(16)	341(19)	272(15)	-38(14)	-37(12)	89(14)
C(70)	291(17)	244(17)	341(16)	14(14)	-62(13)	50(14)
C(71)	211(15)	239(17)	260(15)	18(13)	-28(12)	-27(12)
C(72)	297(17)	440(20)	279(16)	173(15)	39(13)	26(15)
C(73)	319(17)	490(20)	202(15)	21(15)	45(13)	74(15)
C(74)	228(15)	330(18)	222(14)	-43(13)	-3(12)	14(13)
C(75)	112(13)	274(17)	212(14)	-56(12)	14(11)	-33(12)
C(76)	207(15)	248(18)	367(17)	-7(14)	79(13)	-17(13)
C(77)	222(16)	267(18)	466(19)	-72(15)	66(14)	10(13)
C(78)	203(16)	360(20)	406(18)	-152(15)	111(14)	-33(14)
C(79)	281(16)	340(20)	289(16)	-86(14)	123(13)	-84(14)
C(80)	229(15)	234(17)	278(15)	-47(13)	34(12)	-52(13)
C(81)	210(14)	201(16)	224(14)	-7(12)	23(12)	-30(12)
C(82)	216(16)	570(20)	250(15)	-1(15)	23(13)	-19(15)
C(83)	370(20)	870(30)	219(16)	36(18)	71(15)	-67(19)
C(84)	383(19)	670(30)	219(16)	22(16)	-31(14)	-95(18)
C(85)	254(16)	430(20)	336(17)	16(15)	-63(13)	-51(15)
C(86)	196(15)	299(18)	277(15)	7(13)	34(12)	-37(13)
C(87)	209(14)	250(16)	214(14)	-17(12)	19(11)	-21(12)
C(88)	208(15)	268(17)	244(14)	-11(13)	9(12)	45(13)
C(89)	328(17)	272(18)	370(17)	-66(14)	36(14)	25(14)
C(90)	620(20)	470(20)	388(19)	-129(17)	189(18)	119(19)
C(91)	940(30)	540(20)	298(19)	-102(18)	190(20)	30(20)

C(92)	660(20)	480(20)	303(18)	-43(17)	-131(16)	106(19)
C(93)	348(18)	334(19)	300(16)	-107(14)	-44(14)	99(15)
C(94)	318(18)	500(20)	427(19)	-172(17)	-166(14)	49(17)
C(95)	600(20)	350(20)	490(20)	-160(17)	-152(17)	-34(18)
C(96)	397(19)	320(20)	475(19)	-135(16)	23(16)	43(16)
C(1A)	1470(50)	360(30)	700(30)	140(20)	620(30)	480(30)
C(2A)	890(30)	440(30)	760(30)	-250(20)	270(30)	10(20)
C(3A)	510(20)	580(30)	320(18)	-141(18)	39(17)	116(19)
C(4A)	420(20)	730(30)	365(19)	-107(19)	98(17)	130(20)
C(5A)	440(20)	1120(40)	400(20)	-180(20)	-42(19)	280(20)
C(6A)	990(40)	960(40)	310(20)	-80(20)	20(20)	710(30)
C(1B)	1910(60)	860(40)	620(30)	70(30)	270(40)	-370(40)
C(2B)	1830(60)	700(40)	1010(40)	-30(30)	240(40)	-680(40)
C(3B)	820(30)	670(30)	1080(40)	-190(30)	220(30)	-250(30)
C(4B)	730(30)	610(30)	830(30)	-10(30)	340(30)	50(20)
C(5B)	820(30)	540(30)	690(30)	-120(20)	30(20)	140(20)
C(6B)	980(40)	660(30)	730(30)	-30(30)	100(30)	-150(30)

Table 1. Crystal data and structure refinement for 11 (AJMM55) (CCDC 776949).

Empirical formula	$C_{44}H_{39}BO_{10}P_2Re_2$	
Formula weight	1172.90	
Crystallization Solvent	Dichloromethane/Toluene	
Crystal Habit	Fragment	
Crystal size	0.10 x 0.09 x 0.03 mm^3	
Crystal color	Colorless	

Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 4004 reflections used in lattice determination	2.17 to 22.56°	
Unit cell dimensions	a = 15.776(2) Å	α= 90°
	b = 16.5631(19) Å	β= 90.322(5)°
	c = 16.523(2) Å	γ = 90°
Volume	4317.5(9) $Å^3$	
Z	4	
Crystal system	Monoclinic	
Space group	P $2_1/n$	
Density (calculated)	1.804 Mg/m^3	
F(000)	2272	
Data collection program	Bruker APEX2 v2009.7-0	
θ range for data collection	1.74 to 26.41°	

Completeness to $\theta = 26.41°$	98.1 %
Index ranges	$-19 \le h \le 15, -20 \le k \le 20, -20 \le l \le 19$
Data collection scan type	ω scans; 5 settings
Data reduction program	Bruker SAINT-Plus v7.66A
Reflections collected	34093
Independent reflections	8714 [R_{int}= 0.1185]
Absorption coefficient	5.733 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.5256

Table 1 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	8714 / 12 / 532
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.229
Final R indices [$I>2\sigma(I)$, 4950 reflections]	R1 = 0.0658, *w*R2 = 0.0941
R indices (all data)	R1 = 0.1423, *w*R2 = 0.1068
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Largest diff. peak and hole	1.736 and -1.309 e.Å^{-3}

Special Refinement Details

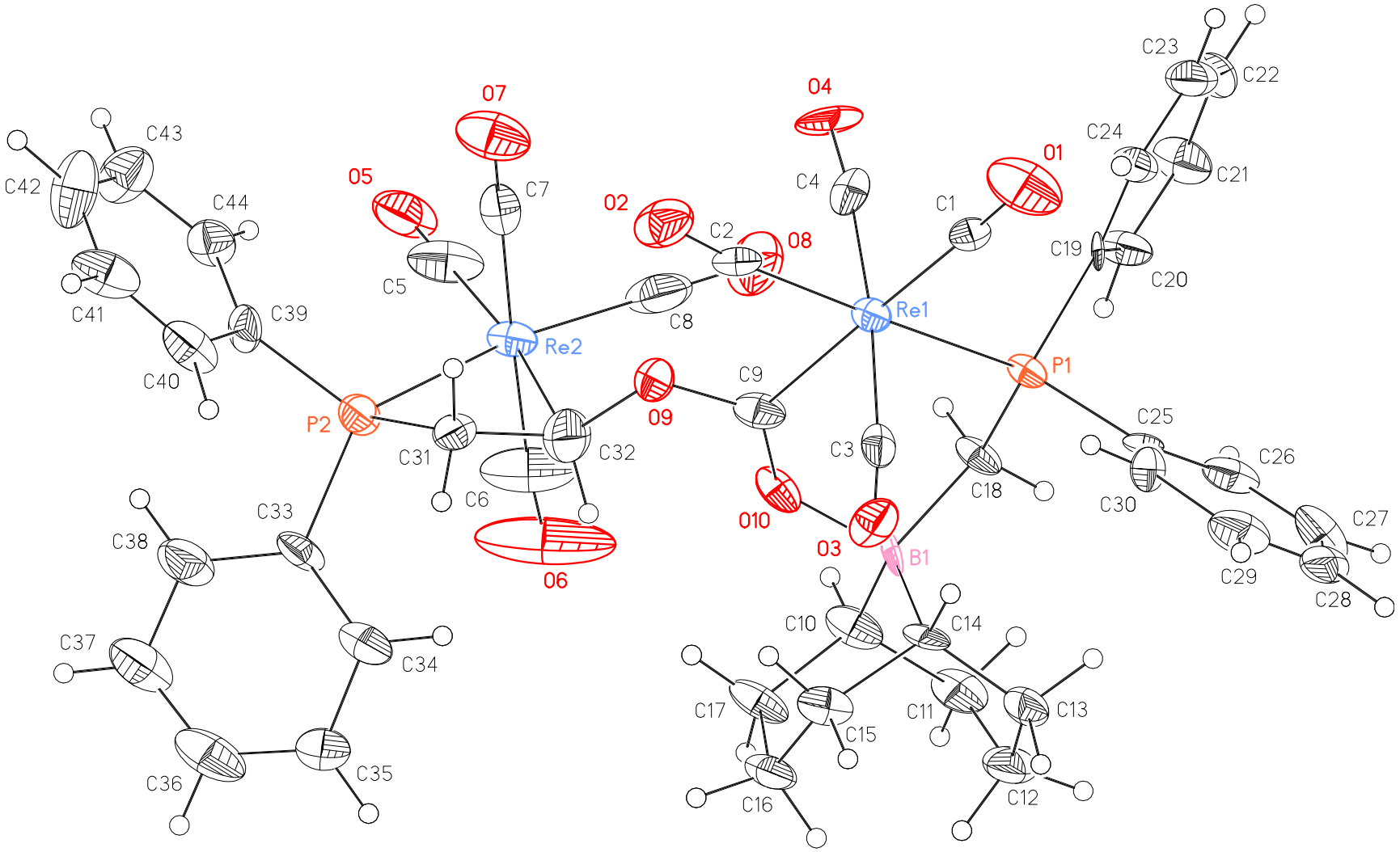
Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

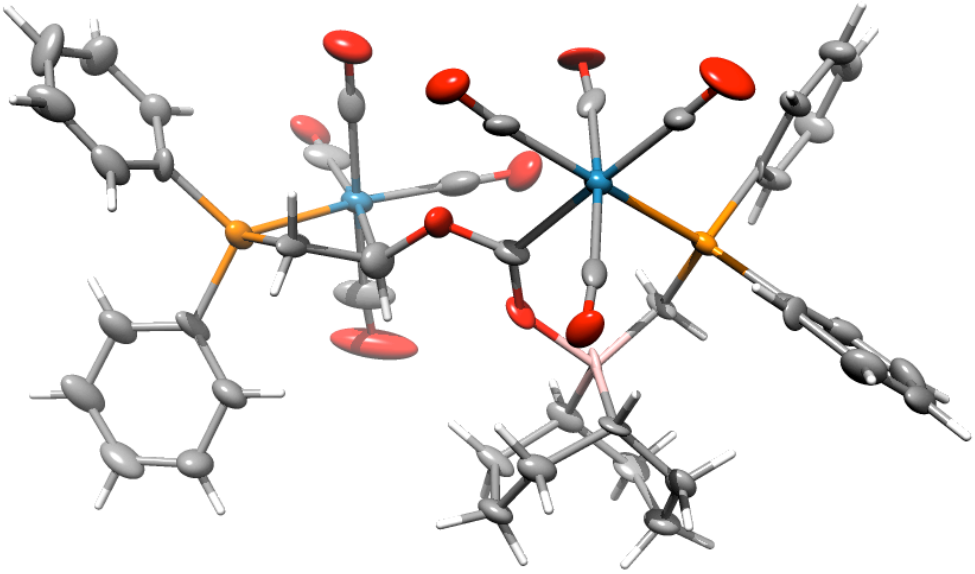
This is a small and weakly diffracting crystal. Restraints were placed on the ADP's of atoms C19 and C25 keep them fro going non-positive definite during refinement.

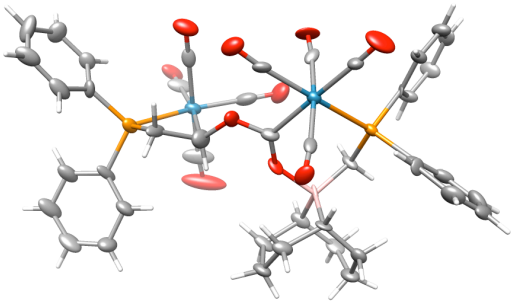
Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will

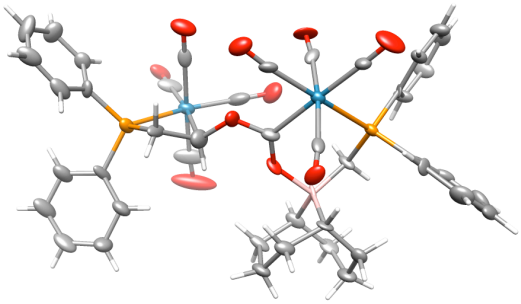
be even larger.

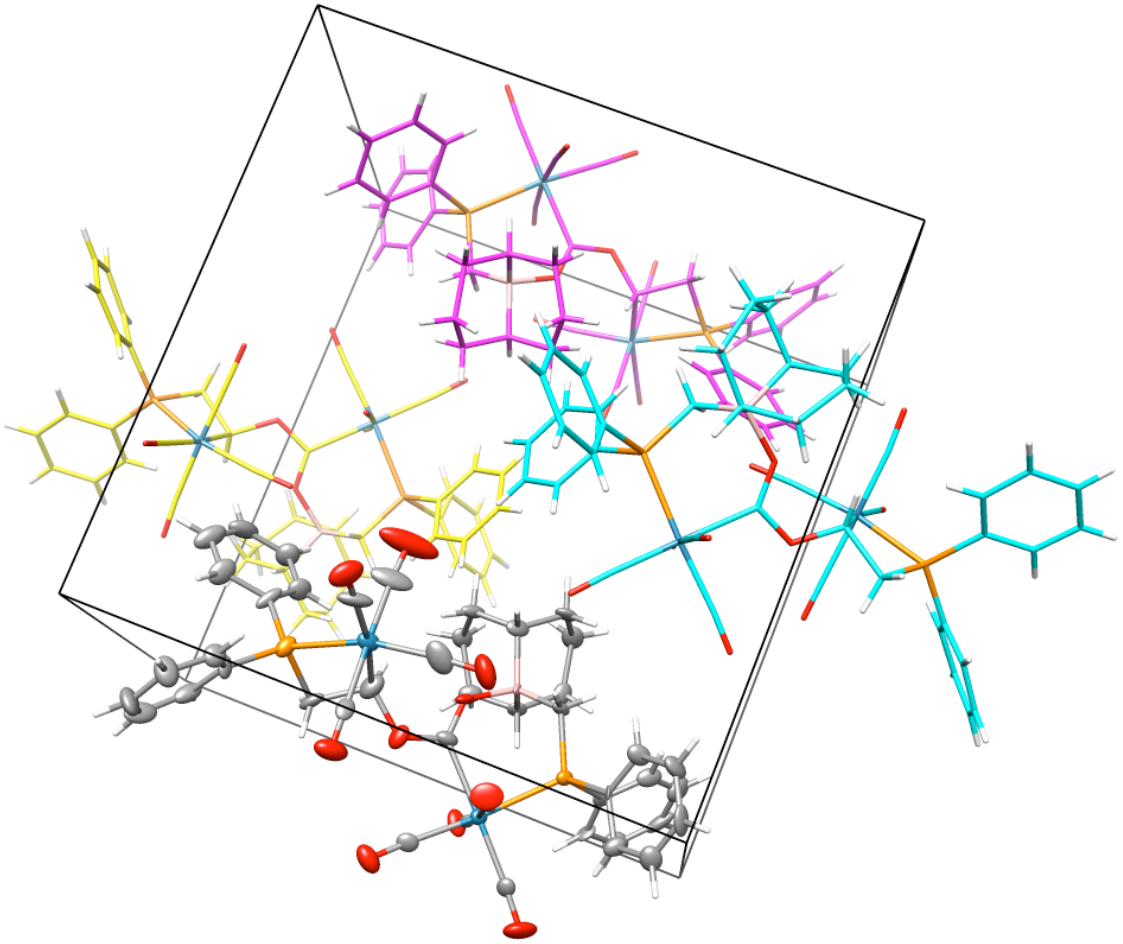
All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

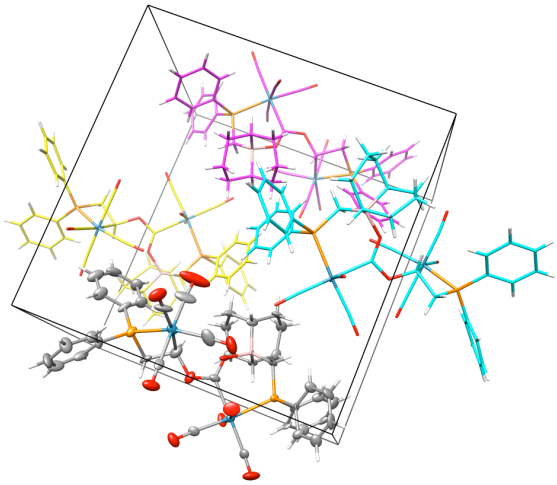

C23
C22
C24
C21
C19
C20
C1
01
04
C4
07
C7
05
C5
02
C2
08
C8
Re1
Re2
P1
P2
C9
09
C25
C26
C30
C27
C29
C28
C3
C18
010
03
B1
C10
C14
C17
C15
C11
C13
C16
C12
C31
C32
C6
C33
C38
C37
C34
C36
C35
C39
C44
C43
C42
C41
C40











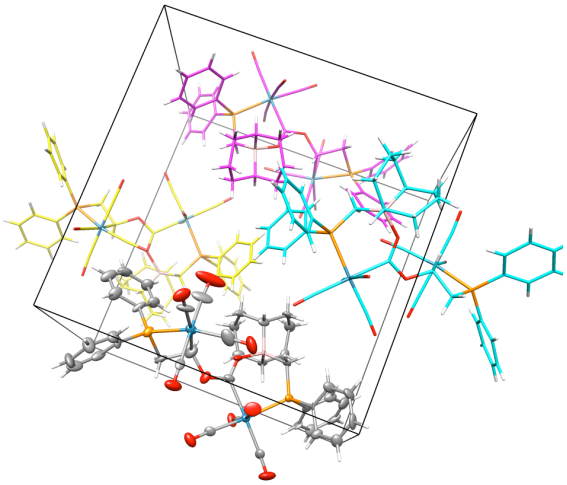


Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 11 (AJMM55) (CCDC 776949). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Re(1)	6728(1)	10615(1)	6770(1)	21(1)
Re(2)	8595(1)	8846(1)	4369(1)	28(1)
P(1)	6569(2)	9536(2)	7797(2)	20(1)
P(2)	7988(2)	9338(2)	3095(2)	29(1)
O(1)	6538(6)	12008(5)	8023(6)	62(3)
O(2)	7207(6)	11874(5)	5452(6)	46(3)
O(3)	4811(5)	10761(4)	6286(5)	36(2)
O(4)	8691(5)	10374(5)	6954(6)	45(3)
O(5)	10382(6)	8206(5)	3971(6)	53(3)
O(6)	7907(7)	7114(6)	4256(9)	127(7)
O(7)	9235(6)	10617(5)	4576(6)	52(3)
O(8)	8780(6)	8647(5)	6239(6)	61(3)
O(9)	7154(5)	9938(5)	5168(5)	34(2)
O(10)	6547(5)	8952(4)	5845(4)	26(2)
B(1)	6062(9)	8448(7)	6519(7)	19(3)
C(1)	6614(8)	11473(6)	7575(7)	27(3)
C(2)	7002(7)	11407(6)	5905(8)	27(3)
C(3)	5511(9)	10700(6)	6504(7)	27(3)
C(4)	7953(8)	10470(5)	6924(7)	25(3)
C(5)	9707(9)	8442(7)	4122(9)	45(4)
C(6)	8134(9)	7765(8)	4258(11)	65(5)
C(7)	9012(7)	9962(7)	4505(7)	28(3)
C(8)	8731(9)	8691(8)	5502(10)	54(5)
C(9)	6805(8)	9664(6)	5844(8)	28(3)

C(10)	6109(8)	7521(6)	6157(7)	33(4)
C(11)	5660(8)	6965(6)	6777(8)	35(4)
C(12)	4756(8)	7167(6)	6937(8)	41(4)
C(13)	4603(8)	8095(6)	7114(7)	31(3)
C(14)	5080(7)	8665(6)	6546(7)	24(3)
C(15)	4727(7)	8673(6)	5681(7)	33(3)
C(16)	4828(8)	7863(6)	5212(7)	34(4)
C(17)	5723(8)	7487(6)	5325(7)	33(4)
C(18)	6616(7)	8539(5)	7342(6)	25(3)
C(19)	7416(7)	9570(5)	8567(6)	14(3)
C(20)	7834(7)	8879(6)	8815(7)	33(3)
C(21)	8437(8)	8908(6)	9417(7)	39(4)
C(22)	8617(8)	9630(7)	9789(7)	41(4)
C(23)	8202(8)	10301(7)	9565(8)	38(4)
C(24)	7588(7)	10304(6)	8970(7)	29(3)
C(25)	5636(8)	9544(6)	8428(7)	26(3)
C(26)	5538(8)	8953(7)	9006(8)	34(3)
C(27)	4833(10)	8904(8)	9496(8)	50(4)
C(28)	4180(8)	9472(8)	9400(8)	42(4)
C(29)	4266(9)	10083(8)	8839(8)	45(4)
C(30)	5009(7)	10135(6)	8354(7)	26(3)
C(31)	7207(8)	9927(6)	3665(7)	33(3)
C(32)	7266(9)	9368(8)	4477(8)	46(4)
C(33)	7386(8)	8673(7)	2419(8)	33(3)
C(34)	6677(8)	8288(6)	2681(8)	38(4)
C(35)	6200(9)	7779(7)	2177(9)	43(4)
C(36)	6494(10)	7686(7)	1391(9)	52(5)
C(37)	7190(9)	8081(8)	1094(9)	52(4)
C(38)	7642(8)	8576(7)	1608(8)	45(4)

C(39)	8573(8)	10016(6)	2455(7)	27(3)
C(40)	8175(8)	10578(7)	1988(7)	38(4)
C(41)	8648(9)	11142(7)	1534(9)	44(4)
C(42)	9510(10)	11073(7)	1523(8)	54(4)
C(43)	9907(9)	10476(7)	1954(8)	46(4)
C(44)	9439(8)	9965(7)	2429(7)	32(3)

Table 3. Selected bond lengths [Å] and angles [°] for 11 (AJMM55) (CCDC 776949).

Re(1)-C(1)	1.955(12)	C(1)-Re(1)-C(4)	95.5(5)
Re(1)-C(4)	1.963(13)	C(1)-Re(1)-C(3)	90.4(5)
Re(1)-C(3)	1.973(13)	C(4)-Re(1)-C(3)	173.8(5)
Re(1)-C(2)	1.990(13)	C(1)-Re(1)-C(2)	91.8(5)
Re(1)-C(9)	2.200(11)	C(4)-Re(1)-C(2)	87.5(5)
Re(1)-P(1)	2.478(3)	C(3)-Re(1)-C(2)	90.5(5)
Re(2)-C(8)	1.900(16)	C(1)-Re(1)-C(9)	177.6(4)
Re(2)-C(5)	1.924(15)	C(4)-Re(1)-C(9)	86.8(4)
Re(2)-C(6)	1.942(13)	C(3)-Re(1)-C(9)	87.3(4)
Re(2)-C(7)	1.974(12)	C(2)-Re(1)-C(9)	87.6(5)
Re(2)-C(32)	2.277(13)	C(1)-Re(1)-P(1)	92.8(3)
Re(2)-P(2)	2.448(3)	C(4)-Re(1)-P(1)	85.8(3)
		C(3)-Re(1)-P(1)	95.8(3)
		C(2)-Re(1)-P(1)	172.2(4)
		C(9)-Re(1)-P(1)	88.1(3)
		C(8)-Re(2)-C(5)	93.7(6)
		C(8)-Re(2)-C(6)	90.5(6)
		C(5)-Re(2)-C(6)	90.0(5)
		C(8)-Re(2)-C(7)	88.8(5)
		C(5)-Re(2)-C(7)	92.7(5)
		C(6)-Re(2)-C(7)	177.2(6)
		C(8)-Re(2)-C(32)	94.2(6)
		C(5)-Re(2)-C(32)	172.1(6)
		C(6)-Re(2)-C(32)	90.7(5)
		C(7)-Re(2)-C(32)	86.7(5)
		C(8)-Re(2)-P(2)	159.0(5)
		C(5)-Re(2)-P(2)	106.6(5)

C(6)-Re(2)-P(2)	94.7(4)	C(32)-Re(2)-P(2)	65.5(3)
C(7)-Re(2)-P(2)	85.1(3)		

Table 4. Bond lengths [Å] and angles [°] for 11 (AJMM55) (CCDC 776949).

Re(1)-C(1)	1.955(12)	O(9)-C(32)	1.493(13)
Re(1)-C(4)	1.963(13)	O(10)-C(9)	1.248(11)
Re(1)-C(3)	1.973(13)	O(10)-B(1)	1.591(15)
Re(1)-C(2)	1.990(13)	B(1)-C(14)	1.592(17)
Re(1)-C(9)	2.200(11)	B(1)-C(18)	1.619(14)
Re(1)-P(1)	2.478(3)	B(1)-C(10)	1.650(14)
Re(2)-C(8)	1.900(16)	C(10)-C(17)	1.502(13)
Re(2)-C(5)	1.924(15)	C(10)-C(11)	1.551(16)
Re(2)-C(6)	1.942(13)	C(11)-C(12)	1.490(17)
Re(2)-C(7)	1.974(12)	C(12)-C(13)	1.583(14)
Re(2)-C(32)	2.277(13)	C(13)-C(14)	1.532(15)
Re(2)-P(2)	2.448(3)	C(14)-C(15)	1.530(14)
P(1)-C(25)	1.809(13)	C(15)-C(16)	1.558(13)
P(1)-C(18)	1.816(9)	C(16)-C(17)	1.553(15)
P(1)-C(19)	1.840(10)	C(19)-C(20)	1.382(13)
P(2)-C(39)	1.801(12)	C(19)-C(24)	1.412(12)
P(2)-C(33)	1.830(11)	C(20)-C(21)	1.373(13)
P(2)-C(31)	1.836(12)	C(21)-C(22)	1.373(14)
O(1)-C(1)	1.161(12)	C(22)-C(23)	1.341(14)
O(2)-C(2)	1.124(13)	C(23)-C(24)	1.376(14)
O(3)-C(3)	1.164(13)	C(25)-C(26)	1.377(15)
O(4)-C(4)	1.175(13)	C(25)-C(30)	1.397(15)
O(5)-C(5)	1.162(15)	C(26)-C(27)	1.383(18)
O(6)-C(6)	1.135(13)	C(27)-C(28)	1.404(16)
O(7)-C(7)	1.147(12)	C(28)-C(29)	1.380(16)
O(8)-C(8)	1.222(16)	C(29)-C(30)	1.426(17)
O(9)-C(9)	1.328(14)	C(31)-C(32)	1.632(16)

C(33)-C(34)	1.360(17)	C(8)-Re(2)-C(6)	90.5(6)
C(33)-C(38)	1.411(17)	C(5)-Re(2)-C(6)	90.0(5)
C(34)-C(35)	1.402(14)	C(8)-Re(2)-C(7)	88.8(5)
C(35)-C(36)	1.389(19)	C(5)-Re(2)-C(7)	92.7(5)
C(36)-C(37)	1.371(19)	C(6)-Re(2)-C(7)	177.2(6)
C(37)-C(38)	1.377(15)	C(8)-Re(2)-C(32)	94.2(6)
C(39)-C(40)	1.360(14)	C(5)-Re(2)-C(32)	172.1(6)
C(39)-C(44)	1.370(16)	C(6)-Re(2)-C(32)	90.7(5)
C(40)-C(41)	1.414(18)	C(7)-Re(2)-C(32)	86.7(5)
C(41)-C(42)	1.364(18)	C(8)-Re(2)-P(2)	159.0(5)
C(42)-C(43)	1.368(15)	C(5)-Re(2)-P(2)	106.6(5)
C(43)-C(44)	1.372(16)	C(6)-Re(2)-P(2)	94.7(4)
		C(7)-Re(2)-P(2)	85.1(3)
C(1)-Re(1)-C(4)	95.5(5)	C(32)-Re(2)-P(2)	65.5(3)
C(1)-Re(1)-C(3)	90.4(5)	C(25)-P(1)-C(18)	106.3(5)
C(4)-Re(1)-C(3)	173.8(5)	C(25)-P(1)-C(19)	101.1(5)
C(1)-Re(1)-C(2)	91.8(5)	C(18)-P(1)-C(19)	106.4(4)
C(4)-Re(1)-C(2)	87.5(5)	C(25)-P(1)-Re(1)	118.4(4)
C(3)-Re(1)-C(2)	90.5(5)	C(18)-P(1)-Re(1)	111.6(4)
C(1)-Re(1)-C(9)	177.6(4)	C(19)-P(1)-Re(1)	112.0(3)
C(4)-Re(1)-C(9)	86.8(4)	C(39)-P(2)-C(33)	106.5(6)
C(3)-Re(1)-C(9)	87.3(4)	C(39)-P(2)-C(31)	108.5(5)
C(2)-Re(1)-C(9)	87.6(5)	C(33)-P(2)-C(31)	106.6(5)
C(1)-Re(1)-P(1)	92.8(3)	C(39)-P(2)-Re(2)	120.9(4)
C(4)-Re(1)-P(1)	85.8(3)	C(33)-P(2)-Re(2)	121.6(4)
C(3)-Re(1)-P(1)	95.8(3)	C(31)-P(2)-Re(2)	89.7(4)
C(2)-Re(1)-P(1)	172.2(4)	C(9)-O(9)-C(32)	118.6(9)
C(9)-Re(1)-P(1)	88.1(3)	C(9)-O(10)-B(1)	130.9(9)
C(8)-Re(2)-C(5)	93.7(6)	C(14)-B(1)-O(10)	111.9(8)

C(14)-B(1)-C(18)	118.5(10)	C(20)-C(19)-C(24)	118.8(9)
O(10)-B(1)-C(18)	106.3(9)	C(20)-C(19)-P(1)	121.6(7)
C(14)-B(1)-C(10)	105.4(9)	C(24)-C(19)-P(1)	119.3(7)
O(10)-B(1)-C(10)	102.2(9)	C(21)-C(20)-C(19)	120.9(10)
C(18)-B(1)-C(10)	111.5(8)	C(20)-C(21)-C(22)	119.7(10)
O(1)-C(1)-Re(1)	176.7(10)	C(23)-C(22)-C(21)	119.9(10)
O(2)-C(2)-Re(1)	174.7(10)	C(22)-C(23)-C(24)	122.7(11)
O(3)-C(3)-Re(1)	174.7(11)	C(23)-C(24)-C(19)	117.8(10)
O(4)-C(4)-Re(1)	174.9(11)	C(26)-C(25)-C(30)	118.6(13)
O(5)-C(5)-Re(2)	179.3(13)	C(26)-C(25)-P(1)	119.2(10)
O(6)-C(6)-Re(2)	173.6(14)	C(30)-C(25)-P(1)	122.2(9)
O(7)-C(7)-Re(2)	178.3(10)	C(25)-C(26)-C(27)	122.8(12)
O(8)-C(8)-Re(2)	174.8(13)	C(26)-C(27)-C(28)	119.1(14)
O(10)-C(9)-O(9)	117.4(11)	C(29)-C(28)-C(27)	119.5(14)
O(10)-C(9)-Re(1)	131.1(10)	C(28)-C(29)-C(30)	120.4(12)
O(9)-C(9)-Re(1)	111.4(7)	C(25)-C(30)-C(29)	119.5(11)
C(17)-C(10)-C(11)	113.5(10)	C(32)-C(31)-P(2)	94.9(7)
C(17)-C(10)-B(1)	110.4(8)	O(9)-C(32)-C(31)	105.3(9)
C(11)-C(10)-B(1)	107.0(10)	O(9)-C(32)-Re(2)	114.4(8)
C(12)-C(11)-C(10)	115.0(9)	C(31)-C(32)-Re(2)	101.5(8)
C(11)-C(12)-C(13)	113.4(9)	C(34)-C(33)-C(38)	119.3(11)
C(14)-C(13)-C(12)	114.1(10)	C(34)-C(33)-P(2)	120.9(11)
C(15)-C(14)-C(13)	113.6(8)	C(38)-C(33)-P(2)	119.8(11)
C(15)-C(14)-B(1)	109.0(10)	C(33)-C(34)-C(35)	122.1(13)
C(13)-C(14)-B(1)	111.0(9)	C(36)-C(35)-C(34)	116.2(14)
C(14)-C(15)-C(16)	114.9(8)	C(37)-C(36)-C(35)	123.6(13)
C(17)-C(16)-C(15)	112.4(8)	C(36)-C(37)-C(38)	118.4(15)
C(10)-C(17)-C(16)	117.3(11)	C(37)-C(38)-C(33)	120.3(14)
B(1)-C(18)-P(1)	114.2(7)	C(40)-C(39)-C(44)	118.8(12)

C(40)-C(39)-P(2)	121.6(10)
C(44)-C(39)-P(2)	119.6(9)
C(39)-C(40)-C(41)	120.6(12)
C(42)-C(41)-C(40)	118.8(12)
C(41)-C(42)-C(43)	120.5(14)
C(42)-C(43)-C(44)	119.8(13)
C(39)-C(44)-C(43)	121.3(11)

Table 5. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for 11 (AJMM55) (CCDC 776949). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

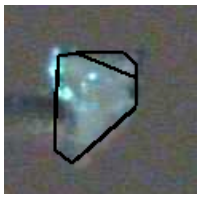
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Re(1)	212(3)	206(2)	216(3)	-6(2)	-37(2)	-15(2)
Re(2)	253(3)	244(3)	342(3)	-4(2)	-87(3)	-33(2)
P(1)	220(18)	191(15)	190(18)	-23(12)	-68(15)	-2(13)
P(2)	209(19)	408(18)	250(20)	-78(16)	6(16)	9(16)
O(1)	810(90)	330(50)	710(80)	-260(50)	-160(70)	-20(50)
O(2)	410(60)	420(50)	540(70)	190(50)	-70(50)	-110(50)
O(3)	180(50)	510(50)	390(60)	200(40)	-30(50)	30(40)
O(4)	90(50)	530(60)	720(80)	-100(50)	-20(50)	-110(40)
O(5)	400(70)	640(60)	540(70)	-280(50)	-90(60)	-30(50)
O(6)	750(100)	360(60)	2680(180)	-90(80)	-920(110)	-20(60)
O(7)	550(70)	290(50)	710(70)	-70(50)	-230(60)	0(50)
O(8)	660(80)	660(70)	520(70)	300(60)	-10(60)	-130(60)
O(9)	250(50)	500(50)	270(60)	-70(40)	80(40)	-60(40)
O(10)	410(50)	130(40)	230(50)	-80(30)	-90(40)	70(40)
B(1)	400(100)	130(60)	50(70)	10(50)	-20(70)	90(60)
C(1)	300(80)	250(60)	270(80)	0(60)	0(70)	-130(60)
C(2)	200(70)	260(70)	360(90)	-30(60)	-50(70)	-90(60)
C(3)	490(90)	140(60)	180(70)	-50(50)	70(70)	-100(60)
C(4)	380(90)	80(50)	300(80)	20(50)	120(70)	-10(60)
C(5)	360(90)	180(60)	800(120)	-160(70)	-160(90)	60(70)
C(6)	320(100)	290(80)	1340(160)	-50(90)	-310(100)	90(70)
C(7)	220(70)	380(70)	240(80)	20(60)	-10(60)	160(60)
C(8)	410(100)	550(90)	670(120)	200(80)	-140(90)	-260(70)
C(9)	310(80)	160(60)	370(90)	-20(50)	-100(70)	-20(50)

C(10)	350(90)	250(60)	390(90)	-40(60)	-200(70)	80(60)
C(11)	520(100)	110(60)	410(90)	-40(50)	-130(80)	-30(60)
C(12)	480(100)	360(70)	400(90)	-20(60)	-110(80)	-210(70)
C(13)	240(80)	430(70)	260(80)	-10(60)	-100(60)	-10(60)
C(14)	260(70)	170(60)	290(80)	-80(50)	-100(60)	-80(50)
C(15)	270(80)	290(70)	440(90)	-90(60)	-70(70)	10(60)
C(16)	380(90)	300(60)	330(80)	-10(60)	-160(70)	-100(60)
C(17)	430(90)	170(60)	390(80)	-100(60)	-240(70)	90(60)
C(18)	420(80)	100(50)	230(70)	-10(50)	-150(70)	-20(50)
C(19)	220(60)	180(50)	40(50)	50(40)	30(50)	10(40)
C(20)	310(80)	280(60)	400(90)	10(60)	-160(70)	-60(60)
C(21)	500(100)	250(60)	410(90)	100(60)	-240(80)	-10(70)
C(22)	400(90)	610(90)	220(80)	170(60)	-170(70)	-120(70)
C(23)	380(90)	390(70)	380(90)	40(60)	-100(80)	-180(70)
C(24)	230(80)	340(70)	290(80)	-100(60)	-20(70)	-40(60)
C(25)	270(60)	270(50)	230(60)	-90(50)	-30(50)	-190(50)
C(26)	240(80)	360(70)	420(90)	-130(70)	-130(70)	10(60)
C(27)	590(110)	600(90)	290(90)	-90(70)	-170(90)	40(90)
C(28)	290(80)	590(90)	380(90)	-330(80)	110(70)	-140(80)
C(29)	320(90)	540(90)	500(110)	-70(80)	-170(80)	10(70)
C(30)	240(70)	320(70)	220(80)	-110(60)	110(60)	40(60)
C(31)	310(80)	330(70)	340(80)	-220(60)	150(70)	-130(60)
C(32)	450(100)	550(80)	390(90)	-130(80)	130(70)	-60(80)
C(33)	160(70)	550(80)	280(90)	-250(60)	-40(60)	60(60)
C(34)	410(100)	390(70)	350(90)	-70(60)	-140(80)	-50(70)
C(35)	440(100)	410(80)	440(100)	-70(70)	-20(80)	-150(70)
C(36)	720(130)	260(70)	570(120)	-110(70)	-320(110)	30(80)
C(37)	370(100)	700(100)	490(110)	-290(80)	-130(90)	140(80)
C(38)	310(90)	640(90)	400(100)	-140(70)	-110(80)	30(70)

C(39)	270(80)	380(70)	170(70)	100(60)	-20(60)	50(60)
C(40)	320(90)	470(80)	360(90)	-180(70)	-100(70)	180(70)
C(41)	330(90)	400(80)	600(110)	-130(80)	-200(80)	140(70)
C(42)	750(120)	430(80)	460(100)	260(70)	170(90)	170(80)
C(43)	310(90)	560(90)	530(100)	160(80)	20(80)	50(70)
C(44)	260(80)	380(70)	330(90)	20(60)	-60(70)	60(60)

Table 1. Crystal data and structure refinement for $[Na(THF)_3][3\text{-}M_1]$ (AJMM64) (CCDC 781654).

Empirical formula	$[C_{26}H_{28}BO_5PRe]^+ [Na]^- \bullet 3(C_4H_8O)$
Formula weight	887.77
Crystallization Solvent	Pentane/deuterobenzene
Crystal Habit	Fragment
Crystal size	0.17 x 0.11 x 0.02 mm^3
Crystal color	Colorless



Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 9975 reflections used in lattice determination	2.24 to 25.40°	
Unit cell dimensions	a = 11.6537(4) Å	α= 90°
	b = 27.6665(9) Å	β= 96.479(2)°
	c = 12.1243(4) Å	γ = 90°
Volume	3884.1(2) $Å^3$	
Z	4	
Crystal system	Monoclinic	
Space group	P $2_1/n$	
Density (calculated)	1.518 Mg/m^3	
F(000)	1800	
Data collection program	Bruker APEX2 v2009.7-0	

θ range for data collection	1.84 to 27.72°
Completeness to θ = 27.72°	89.9 %
Index ranges	$-14 \leq h \leq 14, -35 \leq k \leq 34, -14 \leq l \leq 15$
Data collection scan type	ω scans; 8 settings
Data reduction program	Bruker SAINT-Plus v7.66A
Reflections collected	52817
Independent reflections	8198 [R_{int}= 0.0646]
Absorption coefficient	3.230 mm^{-1}
Absorption correction	Gaussian
Max. and min. transmission	0.8575 and 0.6782

Table 1 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	8198 / 0 / 451
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.487
Final R indices [I>2σ(I), 6185 reflections]	R1 = 0.0401, *w*R2 = 0.0514
R indices (all data)	R1 = 0.0624, *w*R2 = 0.0528
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.002
Average shift/error	0.000
Largest diff. peak and hole	1.870 and -2.359 e.Å^{-3}

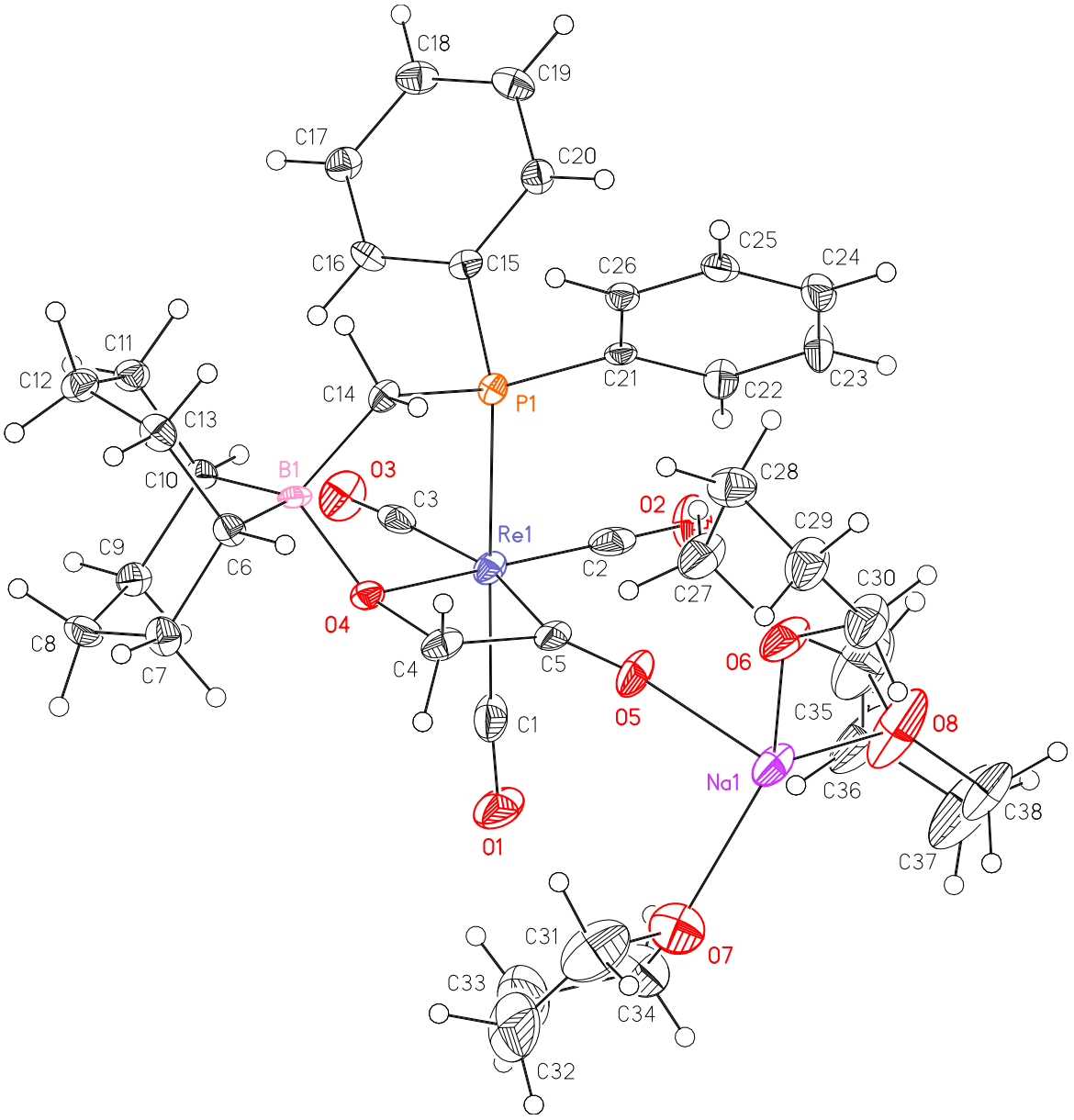
Special Refinement Details

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full

covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.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C13
B1
03
C28
C10
C3
02
Re1
C29
C9
C6
C2
C27
C30
04
C8
C4
C5
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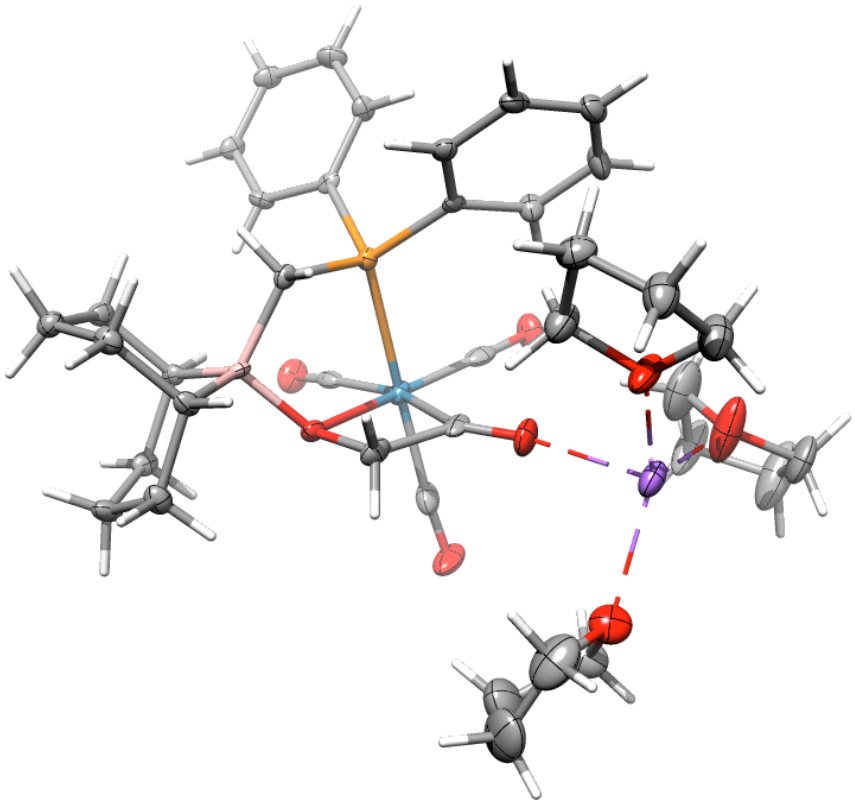
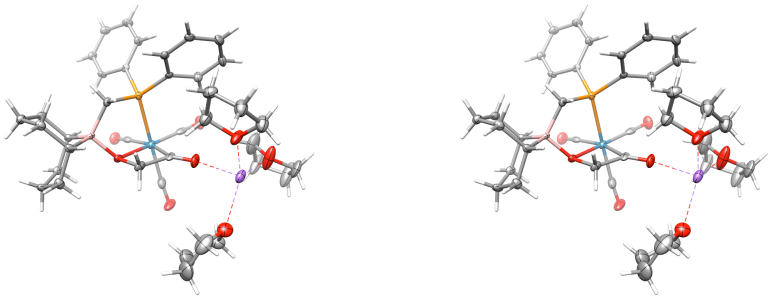
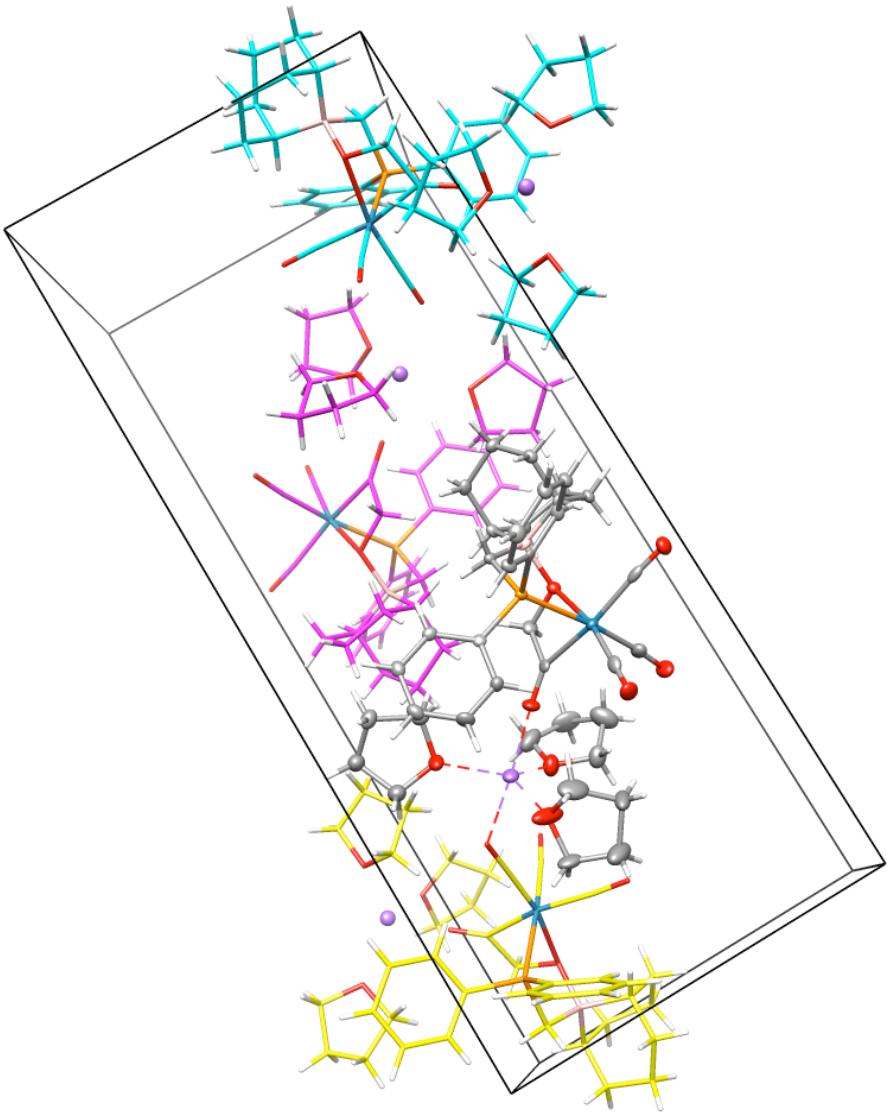
C34
C32







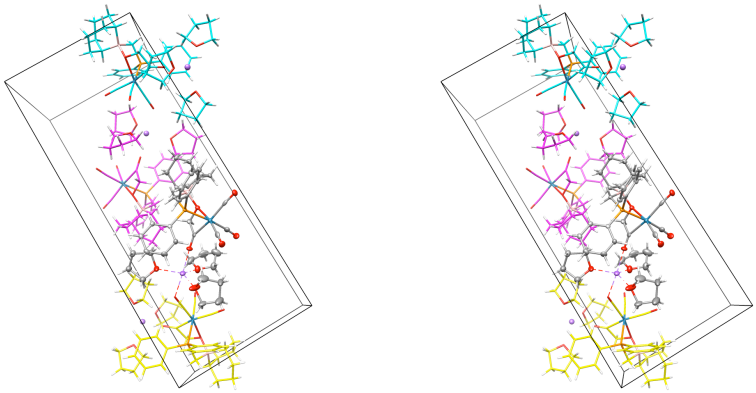


Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [Na(THF)$_3$][3-M$_1$] (AJMM64) (CCDC 781654). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Re(1)	2791(1)	3559(1)	2115(1)	16(1)
P(1)	3896(1)	4127(1)	1068(1)	14(1)
Na(1)	6474(2)	2740(1)	4390(1)	28(1)
O(1)	1769(3)	2847(1)	3710(3)	39(1)
O(2)	2932(3)	2714(1)	519(3)	32(1)
O(3)	356(3)	3808(1)	909(3)	31(1)
O(4)	3087(2)	4161(1)	3308(2)	16(1)
O(5)	5107(3)	3232(1)	3579(3)	29(1)
O(6)	7883(3)	3244(1)	3973(3)	35(1)
O(7)	5498(3)	2672(1)	5948(3)	39(1)
O(8)	6166(3)	2145(1)	3094(3)	66(1)
B(1)	3159(4)	4696(2)	2878(4)	15(1)
C(1)	2111(4)	3126(2)	3114(4)	28(1)
C(2)	2868(4)	3046(2)	1151(4)	25(1)
C(3)	1287(4)	3731(1)	1342(4)	21(1)
C(4)	4114(4)	3962(2)	3914(3)	22(1)
C(5)	4310(3)	3501(2)	3262(3)	19(1)
C(6)	3635(4)	5059(1)	3874(3)	16(1)
C(7)	2884(4)	5004(2)	4840(3)	20(1)
C(8)	1586(4)	5083(2)	4518(3)	23(1)
C(9)	1113(3)	4826(2)	3438(3)	18(1)
C(10)	1866(3)	4871(1)	2473(3)	14(1)
C(11)	1898(4)	5386(1)	1999(3)	19(1)
C(12)	2526(3)	5761(1)	2784(3)	20(1)

C(13)	3662(4)	5577(1)	3419(3)	20(1)
C(14)	4076(3)	4670(1)	1916(3)	15(1)
C(15)	3261(3)	4327(1)	-311(3)	13(1)
C(16)	2177(4)	4546(1)	-425(3)	16(1)
C(17)	1664(4)	4705(1)	-1441(3)	19(1)
C(18)	2232(4)	4646(2)	-2375(4)	22(1)
C(19)	3298(4)	4432(2)	-2281(4)	23(1)
C(20)	3820(4)	4275(1)	-1255(3)	17(1)
C(21)	5324(4)	3922(1)	788(3)	14(1)
C(22)	5499(4)	3443(1)	507(3)	21(1)
C(23)	6553(4)	3286(2)	234(4)	27(1)
C(24)	7467(4)	3602(2)	256(3)	23(1)
C(25)	7316(4)	4077(2)	540(3)	19(1)
C(26)	6256(4)	4236(2)	794(3)	16(1)
C(27)	7608(4)	3720(2)	3542(4)	35(1)
C(28)	8725(4)	3963(2)	3369(4)	30(1)
C(29)	9603(4)	3680(2)	4144(4)	37(1)
C(30)	9110(4)	3180(2)	4022(4)	40(2)
C(31)	5637(5)	3052(2)	6746(5)	58(2)
C(32)	4576(5)	3049(2)	7340(5)	62(2)
C(33)	3673(5)	2842(2)	6483(5)	64(2)
C(34)	4357(4)	2492(2)	5885(4)	41(2)
C(35)	5277(5)	2215(2)	2158(5)	71(2)
C(36)	4400(4)	1870(2)	2359(5)	62(2)
C(37)	5149(5)	1438(2)	2794(5)	81(2)
C(38)	6281(5)	1633(2)	3192(4)	46(2)

Table 3. Selected bond lengths [Å] and angles [°] for $[Na(THF)_3][3\text{-}M_1]$ (AJMM64) (CCDC 781654).

Re(1)-C(2)	1.849(5)	C(2)-Re(1)-C(3)	89.34(18)
Re(1)-C(3)	1.951(5)	C(2)-Re(1)-C(1)	88.42(19)
Re(1)-C(1)	1.935(5)	C(3)-Re(1)-C(1)	92.41(19)
Re(1)-C(5)	2.130(4)	C(2)-Re(1)-C(5)	105.01(18)
Re(1)-O(4)	2.206(3)	C(3)-Re(1)-C(5)	165.33(17)
Re(1)-P(1)	2.4701(11)	C(1)-Re(1)-C(5)	85.05(18)
		C(2)-Re(1)-O(4)	168.30(15)
		C(3)-Re(1)-O(4)	101.34(14)
		C(1)-Re(1)-O(4)	95.80(15)
		C(5)-Re(1)-O(4)	64.66(13)
		C(2)-Re(1)-P(1)	95.64(14)
		C(3)-Re(1)-P(1)	95.19(12)
		C(1)-Re(1)-P(1)	171.42(15)
		C(5)-Re(1)-P(1)	86.59(11)
		O(4)-Re(1)-P(1)	78.81(7)

Table 4. Bond lengths [Å] and angles [°] for [Na(THF)$_3$][3-M$_1$] (AJMM64) (CCDC 781654).

Re(1)-C(2)	1.849(5)	B(1)-C(10)	1.606(6)
Re(1)-C(3)	1.951(5)	B(1)-C(6)	1.619(6)
Re(1)-C(1)	1.935(5)	B(1)-C(14)	1.671(6)
Re(1)-C(5)	2.130(4)	C(4)-C(5)	1.532(6)
Re(1)-O(4)	2.206(3)	C(6)-C(7)	1.547(5)
Re(1)-P(1)	2.4701(11)	C(6)-C(13)	1.537(5)
P(1)-C(21)	1.825(4)	C(7)-C(8)	1.535(5)
P(1)-C(14)	1.821(4)	C(8)-C(9)	1.536(5)
P(1)-C(15)	1.836(4)	C(9)-C(10)	1.544(5)
Na(1)-O(5)	2.238(3)	C(10)-C(11)	1.540(5)
Na(1)-O(6)	2.254(3)	C(11)-C(12)	1.537(5)
Na(1)-O(8)	2.276(4)	C(12)-C(13)	1.542(5)
Na(1)-O(7)	2.320(4)	C(15)-C(20)	1.386(5)
Na(1)-O(2)#1	2.411(3)	C(15)-C(16)	1.395(5)
O(1)-C(1)	1.160(5)	C(16)-C(17)	1.379(5)
O(2)-C(2)	1.201(5)	C(17)-C(18)	1.384(6)
O(2)-Na(1)#2	2.411(3)	C(18)-C(19)	1.369(6)
O(3)-C(3)	1.170(5)	C(19)-C(20)	1.392(5)
O(4)-C(4)	1.440(4)	C(21)-C(26)	1.390(5)
O(4)-B(1)	1.575(5)	C(21)-C(22)	1.389(5)
O(5)-C(5)	1.218(5)	C(22)-C(23)	1.378(6)
O(6)-C(30)	1.436(5)	C(23)-C(24)	1.376(6)
O(6)-C(27)	1.441(5)	C(24)-C(25)	1.376(6)
O(7)-C(34)	1.414(5)	C(25)-C(26)	1.378(5)
O(7)-C(31)	1.426(6)	C(27)-C(28)	1.501(6)
O(8)-C(38)	1.426(5)	C(28)-C(29)	1.526(6)
O(8)-C(35)	1.461(6)	C(29)-C(30)	1.499(6)

C(31)-C(32)	1.499(7)	O(5)-Na(1)-O(8)	95.05(13)
C(32)-C(33)	1.507(7)	O(6)-Na(1)-O(8)	110.75(16)
C(33)-C(34)	1.492(6)	O(5)-Na(1)-O(7)	90.93(13)
C(35)-C(36)	1.439(7)	O(6)-Na(1)-O(7)	131.99(14)
C(36)-C(37)	1.537(7)	O(8)-Na(1)-O(7)	116.77(15)
C(37)-C(38)	1.456(6)	O(5)-Na(1)-O(2)#1	171.03(14)
		O(6)-Na(1)-O(2)#1	88.02(12)
C(2)-Re(1)-C(3)	89.34(18)	O(8)-Na(1)-O(2)#1	93.51(13)
C(2)-Re(1)-C(1)	88.42(19)	O(7)-Na(1)-O(2)#1	82.80(12)
C(3)-Re(1)-C(1)	92.41(19)	C(2)-O(2)-Na(1)#2	132.0(3)
C(2)-Re(1)-C(5)	105.01(18)	C(4)-O(4)-B(1)	117.0(3)
C(3)-Re(1)-C(5)	165.33(17)	C(4)-O(4)-Re(1)	96.1(2)
C(1)-Re(1)-C(5)	85.05(18)	B(1)-O(4)-Re(1)	120.1(2)
C(2)-Re(1)-O(4)	168.30(15)	C(5)-O(5)-Na(1)	172.1(3)
C(3)-Re(1)-O(4)	101.34(14)	C(30)-O(6)-C(27)	107.9(4)
C(1)-Re(1)-O(4)	95.80(15)	C(30)-O(6)-Na(1)	131.4(3)
C(5)-Re(1)-O(4)	64.66(13)	C(27)-O(6)-Na(1)	120.6(3)
C(2)-Re(1)-P(1)	95.64(14)	C(34)-O(7)-C(31)	109.3(4)
C(3)-Re(1)-P(1)	95.19(12)	C(34)-O(7)-Na(1)	122.0(3)
C(1)-Re(1)-P(1)	171.42(15)	C(31)-O(7)-Na(1)	117.7(3)
C(5)-Re(1)-P(1)	86.59(11)	C(38)-O(8)-C(35)	104.3(4)
O(4)-Re(1)-P(1)	78.81(7)	C(38)-O(8)-Na(1)	130.9(3)
C(21)-P(1)-C(14)	108.15(19)	C(35)-O(8)-Na(1)	118.9(3)
C(21)-P(1)-C(15)	101.93(19)	O(4)-B(1)-C(10)	107.5(3)
C(14)-P(1)-C(15)	105.92(18)	O(4)-B(1)-C(6)	111.3(3)
C(21)-P(1)-Re(1)	115.92(13)	C(10)-B(1)-C(6)	105.8(3)
C(14)-P(1)-Re(1)	105.58(13)	O(4)-B(1)-C(14)	104.7(3)
C(15)-P(1)-Re(1)	118.66(13)	C(10)-B(1)-C(14)	116.8(4)
O(5)-Na(1)-O(6)	91.46(12)	C(6)-B(1)-C(14)	110.8(4)

O(1)-C(1)-Re(1)	175.3(4)	C(26)-C(21)-P(1)	122.3(3)
O(2)-C(2)-Re(1)	179.1(4)	C(22)-C(21)-P(1)	120.3(3)
O(3)-C(3)-Re(1)	175.6(4)	C(23)-C(22)-C(21)	121.3(4)
O(4)-C(4)-C(5)	102.6(3)	C(24)-C(23)-C(22)	120.3(4)
O(5)-C(5)-C(4)	119.9(4)	C(23)-C(24)-C(25)	119.4(4)
O(5)-C(5)-Re(1)	143.2(3)	C(26)-C(25)-C(24)	120.2(4)
C(4)-C(5)-Re(1)	96.5(3)	C(25)-C(26)-C(21)	121.3(4)
C(7)-C(6)-C(13)	113.6(3)	O(6)-C(27)-C(28)	107.4(4)
C(7)-C(6)-B(1)	109.1(3)	C(27)-C(28)-C(29)	102.4(4)
C(13)-C(6)-B(1)	109.3(3)	C(30)-C(29)-C(28)	101.0(4)
C(8)-C(7)-C(6)	114.8(3)	O(6)-C(30)-C(29)	105.0(4)
C(9)-C(8)-C(7)	113.5(4)	O(7)-C(31)-C(32)	106.6(4)
C(8)-C(9)-C(10)	115.4(3)	C(31)-C(32)-C(33)	102.8(5)
C(11)-C(10)-C(9)	113.4(3)	C(34)-C(33)-C(32)	102.2(5)
C(11)-C(10)-B(1)	109.4(3)	O(7)-C(34)-C(33)	107.3(4)
C(9)-C(10)-B(1)	109.7(3)	C(36)-C(35)-O(8)	103.6(5)
C(10)-C(11)-C(12)	115.1(3)	C(35)-C(36)-C(37)	100.8(4)
C(13)-C(12)-C(11)	114.1(3)	C(38)-C(37)-C(36)	106.5(4)
C(12)-C(13)-C(6)	115.9(3)	O(8)-C(38)-C(37)	105.5(4)
B(1)-C(14)-P(1)	112.8(3)		
C(20)-C(15)-C(16)	117.9(4)		
C(20)-C(15)-P(1)	122.8(3)		
C(16)-C(15)-P(1)	119.3(3)		
C(17)-C(16)-C(15)	121.6(4)		
C(16)-C(17)-C(18)	119.6(4)		
C(19)-C(18)-C(17)	119.8(4)		
C(18)-C(19)-C(20)	120.7(4)		
C(15)-C(20)-C(19)	120.4(4)		
C(26)-C(21)-C(22)	117.4(4)		

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+1/2,z+1/2

#2 x-1/2,-y+1/2,z-1/2

Table 5. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for $[Na(THF)_3][3\text{-}M_1]$ (AJMM64) (CCDC 781654). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Re(1)	156(1)	123(1)	211(1)	24(1)	14(1)	-11(1)
P(1)	134(6)	127(6)	150(7)	3(5)	3(5)	9(5)
Na(1)	246(11)	208(10)	372(12)	89(9)	-17(9)	28(8)
O(1)	300(20)	310(20)	570(30)	225(19)	153(19)	0(17)
O(2)	300(20)	214(19)	440(20)	-135(17)	19(18)	-20(16)
O(3)	200(20)	310(20)	390(20)	10(16)	-49(17)	-22(16)
O(4)	169(17)	178(16)	133(17)	37(13)	7(14)	19(14)
O(5)	230(20)	218(18)	410(20)	66(16)	-16(17)	84(15)
O(6)	240(20)	259(19)	540(30)	191(17)	33(18)	-7(16)
O(7)	330(20)	410(20)	420(20)	-12(18)	44(18)	-106(18)
O(8)	820(30)	290(20)	760(30)	-80(20)	-430(30)	150(20)
B(1)	210(30)	130(30)	120(30)	50(20)	40(20)	-10(20)
C(1)	220(30)	210(30)	450(40)	0(30)	100(30)	30(20)
C(2)	170(30)	300(30)	280(30)	150(20)	60(20)	-40(20)
C(3)	340(30)	130(20)	190(30)	-20(20)	140(30)	-80(20)
C(4)	210(30)	230(30)	200(30)	70(20)	-40(20)	0(20)
C(5)	140(20)	160(30)	280(30)	100(20)	80(20)	-30(20)
C(6)	140(30)	210(20)	130(30)	-10(20)	-10(20)	20(20)
C(7)	200(30)	230(30)	170(30)	-40(20)	-10(20)	10(20)
C(8)	250(30)	310(30)	140(30)	40(20)	50(20)	40(20)
C(9)	120(20)	210(30)	200(30)	40(20)	10(20)	10(20)
C(10)	170(30)	120(20)	110(30)	-29(19)	10(20)	-29(19)
C(11)	170(30)	220(30)	180(30)	40(20)	20(20)	20(20)
C(12)	240(30)	160(20)	190(30)	10(20)	10(20)	-20(20)

C(13)	200(30)	200(30)	190(30)	-50(20)	30(20)	-40(20)
C(14)	140(20)	130(20)	180(30)	13(19)	-10(20)	1(19)
C(15)	170(20)	80(20)	130(30)	-18(18)	-20(20)	-56(19)
C(16)	160(30)	210(30)	120(30)	-10(20)	50(20)	-20(20)
C(17)	140(30)	210(30)	200(30)	40(20)	-10(20)	0(20)
C(18)	200(30)	260(30)	180(30)	40(20)	-10(20)	-20(20)
C(19)	260(30)	290(30)	140(30)	-10(20)	40(20)	-30(20)
C(20)	160(30)	200(20)	150(30)	-10(20)	-20(20)	20(20)
C(21)	160(30)	160(20)	90(30)	42(19)	7(19)	10(20)
C(22)	180(30)	170(30)	290(30)	-10(20)	40(20)	-20(20)
C(23)	250(30)	210(30)	360(30)	-60(20)	80(30)	70(20)
C(24)	190(30)	280(30)	230(30)	20(20)	50(20)	50(20)
C(25)	180(30)	250(30)	160(30)	50(20)	40(20)	0(20)
C(26)	210(30)	160(20)	120(30)	9(19)	20(20)	0(20)
C(27)	310(30)	270(30)	460(40)	100(20)	20(30)	0(20)
C(28)	340(30)	280(30)	290(30)	30(20)	40(30)	-70(30)
C(29)	300(30)	260(30)	560(40)	20(30)	60(30)	-10(20)
C(30)	330(40)	270(30)	610(40)	40(30)	90(30)	20(30)
C(31)	650(50)	350(40)	720(50)	70(30)	-110(40)	-170(30)
C(32)	930(60)	360(40)	580(50)	-210(30)	60(40)	90(40)
C(33)	540(50)	740(50)	640(50)	-20(40)	120(40)	230(40)
C(34)	390(40)	430(30)	420(40)	-60(30)	70(30)	-110(30)
C(35)	690(50)	530(40)	820(50)	90(40)	-270(40)	200(40)
C(36)	270(40)	350(40)	1200(60)	350(40)	-160(40)	-70(30)
C(37)	610(40)	340(30)	1370(60)	190(40)	-410(40)	-60(40)
C(38)	530(40)	200(30)	610(40)	90(30)	-90(30)	80(30)

Table 1. Crystal data and structure refinement for $[Na(THF)_3][3\text{-}E_1Ph_1]$ (AJMM48) (CCDC 770346).

Empirical formula	$C_{56}H_{69}BNaO_7P_2Re$	
Formula weight	1136.05	
Crystallization Solvent	THF	
Crystal Habit	Block	
Crystal size	0.21 x 0.21 x 0.19 mm^3	
Crystal color	Colorless	

Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 9088 reflections used in lattice determination	2.39 to 49.03°	
Unit cell dimensions	a = 10.8404(4) Å	α= 80.396(2)°
	b = 12.8132(5) Å	β= 81.298(2)°
	c = 20.4220(7) Å	γ = 65.477(2)°
Volume	2533.91(16) $Å^3$	
Z	2	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.489 Mg/m^3	
F(000)	1164	
Data collection program	Bruker APEX2 v2009.7-0	

θ range for data collection	1.76 to 49.89°
Completeness to θ = 49.89°	99.1 %
Index ranges	$-22 \leq h \leq 23, -27 \leq k \leq 27, -43 \leq l \leq 43$
Data collection scan type	ω scans; 27 settings
Data reduction program	Bruker SAINT-Plus v7.66A
Reflections collected	203272
Independent reflections	52421 [R_{int}= 0.0361]
Absorption coefficient	2.522 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7498 and 0.5909

Table 1 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	52421 / 0 / 613
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.289
Final R indices [I>2σ(I), 46790 reflections]	R1 = 0.0233, *w*R2 = 0.0399
R indices (all data)	R1 = 0.0299, *w*R2 = 0.0407
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.023
Average shift/error	0.000
Largest diff. peak and hole	3.573 and -1.124 e.Å^{-3}

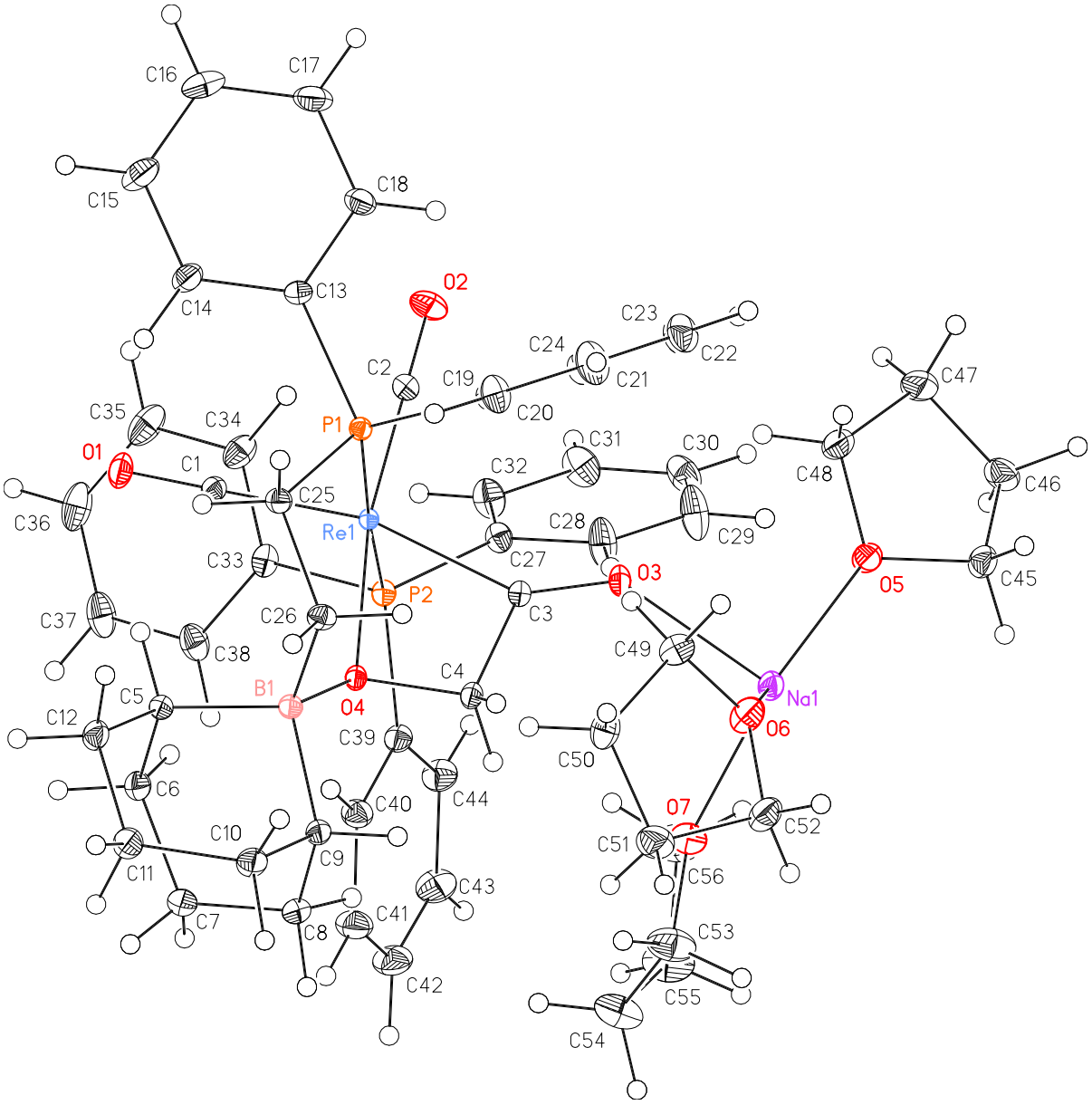
Special Refinement Details

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full

covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.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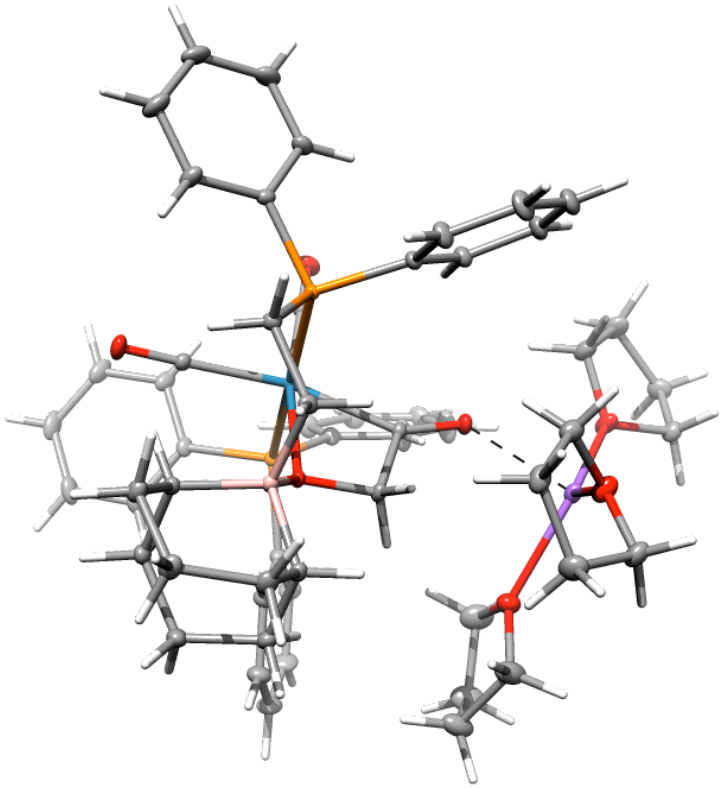
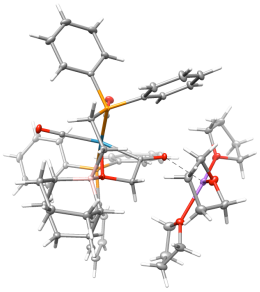
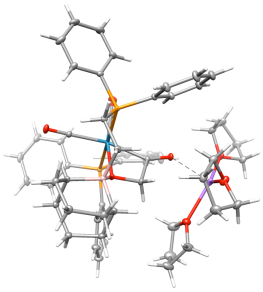
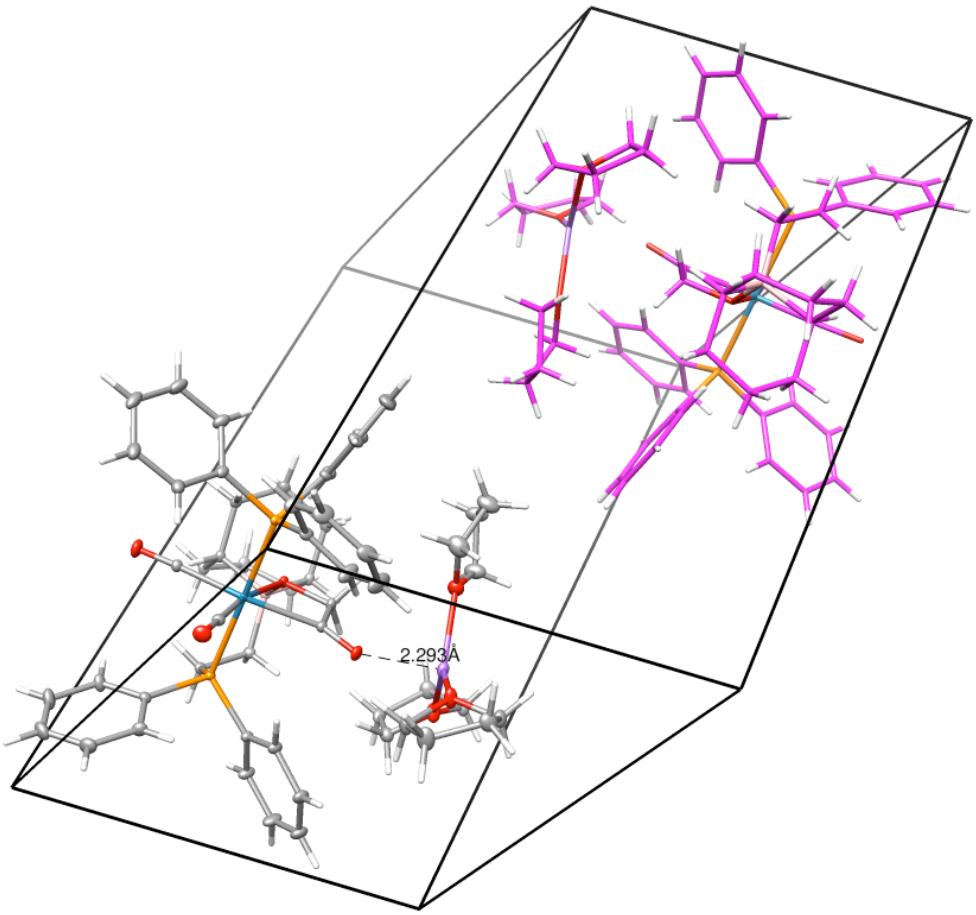
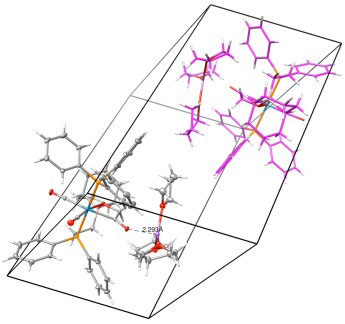
C17
C15
C18
C14
C13
O2
C23
C24
C22
C21
C2
C19
C20
C47
C35
C34
P1
C31
C30
O1
C1
C32
C48
C46
C36
C25
Re1
C28
C29
C27
O3
O5
C45
C33
P2
C3
C37
C26
C49
C38
C4
B1
O4
Na1
C5
C12
C39
O6
C50
C6
C44
C40
O7
C52
C10
C51
C9
C56
C11
C43
C7
C41
C8
C53
C42
C55
C54








2.293Å


2.293Å

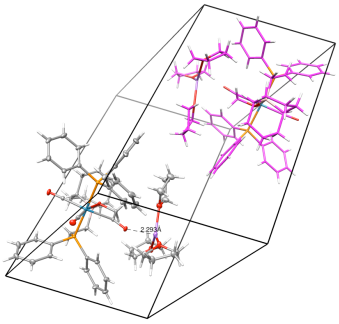

2.293Å

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [$Na(THF)_3$][3-E_1Ph_1] (AJMM48) (CCDC 770346). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Re(1)	8307(1)	6674(1)	7744(1)	7(1)
P(1)	7623(1)	8394(1)	8269(1)	8(1)
P(2)	9031(1)	4829(1)	7327(1)	9(1)
Na(1)	3113(1)	7110(1)	7741(1)	13(1)
O(1)	11150(1)	6783(1)	7445(1)	18(1)
O(2)	9054(1)	5179(1)	9071(1)	18(1)
O(3)	5224(1)	6857(1)	7982(1)	13(1)
O(4)	7378(1)	7816(1)	6833(1)	9(1)
O(5)	3119(1)	5810(1)	8669(1)	18(1)
O(6)	2139(1)	9100(1)	7554(1)	19(1)
O(7)	3896(1)	6686(1)	6674(1)	19(1)
B(1)	7315(1)	9051(1)	6539(1)	9(1)
C(1)	10099(1)	6714(1)	7553(1)	10(1)
C(2)	8763(1)	5760(1)	8564(1)	11(1)
C(3)	6222(1)	7019(1)	7677(1)	10(1)
C(4)	6080(1)	7737(1)	7000(1)	11(1)
C(5)	8843(1)	8917(1)	6232(1)	10(1)
C(6)	9418(1)	8040(1)	5717(1)	13(1)
C(7)	8496(1)	8255(1)	5161(1)	16(1)
C(8)	6963(1)	8648(1)	5384(1)	14(1)
C(9)	6403(1)	9529(1)	5898(1)	11(1)
C(10)	6374(1)	10723(1)	5594(1)	15(1)
C(11)	7782(1)	10771(1)	5416(1)	16(1)
C(12)	8802(1)	10121(1)	5942(1)	14(1)

C(13)	8738(1)	8276(1)	8895(1)	10(1)
C(14)	9801(1)	8649(1)	8728(1)	16(1)
C(15)	10657(1)	8537(1)	9204(1)	21(1)
C(16)	10472(1)	8040(1)	9850(1)	21(1)
C(17)	9435(1)	7646(1)	10018(1)	20(1)
C(18)	8570(1)	7771(1)	9546(1)	15(1)
C(19)	5961(1)	8921(1)	8758(1)	11(1)
C(20)	5198(1)	10097(1)	8810(1)	16(1)
C(21)	3978(1)	10465(1)	9217(1)	20(1)
C(22)	3508(1)	9664(1)	9583(1)	19(1)
C(23)	4251(1)	8495(1)	9531(1)	17(1)
C(24)	5466(1)	8123(1)	9115(1)	13(1)
C(25)	7630(1)	9636(1)	7691(1)	11(1)
C(26)	6693(1)	9905(1)	7134(1)	12(1)
C(27)	8493(1)	3781(1)	7891(1)	12(1)
C(28)	7111(1)	4128(1)	8108(1)	23(1)
C(29)	6616(1)	3343(1)	8480(1)	27(1)
C(30)	7496(1)	2210(1)	8652(1)	20(1)
C(31)	8873(1)	1863(1)	8452(1)	21(1)
C(32)	9369(1)	2643(1)	8071(1)	18(1)
C(33)	10893(1)	4065(1)	7220(1)	12(1)
C(34)	11640(1)	3749(1)	7775(1)	16(1)
C(35)	13057(1)	3230(1)	7701(1)	21(1)
C(36)	13752(1)	3021(1)	7072(1)	22(1)
C(37)	13021(1)	3328(1)	6520(1)	21(1)
C(38)	11603(1)	3848(1)	6589(1)	17(1)
C(39)	8597(1)	4655(1)	6532(1)	12(1)
C(40)	8334(1)	5571(1)	6025(1)	14(1)
C(41)	8168(1)	5424(1)	5385(1)	19(1)

C(42)	8268(1)	4361(1)	5254(1)	21(1)
C(43)	8502(1)	3453(1)	5761(1)	21(1)
C(44)	8661(1)	3594(1)	6400(1)	17(1)
C(45)	2028(1)	5445(1)	8908(1)	16(1)
C(46)	2625(1)	4435(1)	9432(1)	20(1)
C(47)	3577(1)	4779(1)	9749(1)	25(1)
C(48)	3777(1)	5741(1)	9244(1)	19(1)
C(49)	2669(1)	9827(1)	7775(1)	17(1)
C(50)	2770(1)	10683(1)	7168(1)	17(1)
C(51)	2026(1)	10499(1)	6643(1)	22(1)
C(52)	1276(1)	9796(1)	7044(1)	19(1)
C(53)	3458(1)	7300(1)	6042(1)	25(1)
C(54)	4344(1)	6510(1)	5526(1)	26(1)
C(55)	4605(1)	5322(1)	5901(1)	29(1)
C(56)	4708(1)	5485(1)	6603(1)	30(1)

Table 3. Selected bond lengths [Å] and angles [°] for $[Na(THF)_3][3\text{-}E_1Ph_1]$ (AJMM48) (CCDC 770346).

Re(1)-C(2)	1.8799(6)	C(2)-Re(1)-C(1)	92.03(3)
Re(1)-C(1)	1.9428(6)	C(2)-Re(1)-C(3)	105.99(3)
Re(1)-C(3)	2.1361(6)	C(1)-Re(1)-C(3)	161.80(3)
Re(1)-O(4)	2.2470(5)	C(2)-Re(1)-O(4)	169.78(2)
Re(1)-P(1)	2.39823(18)	C(1)-Re(1)-O(4)	97.88(2)
Re(1)-P(2)	2.41937(18)	C(3)-Re(1)-O(4)	64.01(2)
		C(2)-Re(1)-P(1)	90.490(18)
		C(1)-Re(1)-P(1)	87.021(18)
		C(3)-Re(1)-P(1)	90.241(16)
		O(4)-Re(1)-P(1)	87.556(12)
		C(2)-Re(1)-P(2)	83.621(18)
		C(1)-Re(1)-P(2)	93.729(18)
		C(3)-Re(1)-P(2)	90.843(16)
		O(4)-Re(1)-P(2)	98.143(12)
		P(1)-Re(1)-P(2)	174.085(5)

Table 4. Bond lengths [Å] and angles [°] for $[Na(THF)_3][3\text{-}E_1Ph_1]$ (AJMM48) (CCDC 770346).

Re(1)-C(2)	1.8799(6)	O(7)-C(53)	1.4307(11)
Re(1)-C(1)	1.9428(6)	O(7)-C(56)	1.4401(12)
Re(1)-C(3)	2.1361(6)	B(1)-C(5)	1.6289(9)
Re(1)-O(4)	2.2470(5)	B(1)-C(9)	1.6386(9)
Re(1)-P(1)	2.39823(18)	B(1)-C(26)	1.6461(8)
Re(1)-P(2)	2.41937(18)	C(3)-C(4)	1.5181(9)
P(1)-C(25)	1.8182(7)	C(5)-C(6)	1.5407(8)
P(1)-C(19)	1.8350(6)	C(5)-C(12)	1.5417(10)
P(1)-C(13)	1.8357(6)	C(6)-C(7)	1.5408(9)
P(2)-C(39)	1.8289(6)	C(7)-C(8)	1.5420(10)
P(2)-C(33)	1.8380(7)	C(8)-C(9)	1.5423(9)
P(2)-C(27)	1.8432(7)	C(9)-C(10)	1.5420(10)
Na(1)-O(7)	2.2839(6)	C(10)-C(11)	1.5390(10)
Na(1)-O(3)	2.2935(6)	C(11)-C(12)	1.5393(10)
Na(1)-O(5)	2.3030(6)	C(13)-C(18)	1.3984(9)
Na(1)-O(6)	2.3082(7)	C(13)-C(14)	1.3988(10)
Na(1)-O(1)#1	2.5061(6)	C(14)-C(15)	1.3938(10)
O(1)-C(1)	1.1649(8)	C(15)-C(16)	1.3899(12)
O(1)-Na(1)#2	2.5060(6)	C(16)-C(17)	1.3903(13)
O(2)-C(2)	1.1719(8)	C(17)-C(18)	1.3913(10)
O(3)-C(3)	1.2416(8)	C(19)-C(24)	1.3986(9)
O(4)-C(4)	1.4379(8)	C(19)-C(20)	1.3992(9)
O(4)-B(1)	1.5731(9)	C(20)-C(21)	1.3945(10)
O(5)-C(45)	1.4370(9)	C(21)-C(22)	1.3906(12)
O(5)-C(48)	1.4372(9)	C(22)-C(23)	1.3884(11)
O(6)-C(52)	1.4314(10)	C(23)-C(24)	1.3986(9)
O(6)-C(49)	1.4357(9)	C(25)-C(26)	1.5402(9)

C(27)-C(32)	1.3931(10)	C(2)-Re(1)-C(3)	105.99(3)
C(27)-C(28)	1.3973(10)	C(1)-Re(1)-C(3)	161.80(3)
C(28)-C(29)	1.3941(12)	C(2)-Re(1)-O(4)	169.78(2)
C(29)-C(30)	1.3871(14)	C(1)-Re(1)-O(4)	97.88(2)
C(30)-C(31)	1.3847(13)	C(3)-Re(1)-O(4)	64.01(2)
C(31)-C(32)	1.3977(11)	C(2)-Re(1)-P(1)	90.490(18)
C(33)-C(34)	1.3982(10)	C(1)-Re(1)-P(1)	87.021(18)
C(33)-C(38)	1.4042(9)	C(3)-Re(1)-P(1)	90.241(16)
C(34)-C(35)	1.3928(10)	O(4)-Re(1)-P(1)	87.556(12)
C(35)-C(36)	1.3953(12)	C(2)-Re(1)-P(2)	83.621(18)
C(36)-C(37)	1.3842(13)	C(1)-Re(1)-P(2)	93.729(18)
C(37)-C(38)	1.3940(11)	C(3)-Re(1)-P(2)	90.843(16)
C(39)-C(40)	1.3920(10)	O(4)-Re(1)-P(2)	98.143(12)
C(39)-C(44)	1.4016(9)	P(1)-Re(1)-P(2)	174.085(5)
C(40)-C(41)	1.3995(9)	C(25)-P(1)-C(19)	104.76(3)
C(41)-C(42)	1.3888(11)	C(25)-P(1)-C(13)	103.64(3)
C(42)-C(43)	1.3872(13)	C(19)-P(1)-C(13)	100.22(3)
C(43)-C(44)	1.3933(10)	C(25)-P(1)-Re(1)	113.472(19)
C(45)-C(46)	1.5127(11)	C(19)-P(1)-Re(1)	118.84(2)
C(46)-C(47)	1.5350(12)	C(13)-P(1)-Re(1)	114.01(2)
C(47)-C(48)	1.5358(12)	C(39)-P(2)-C(33)	99.89(3)
C(49)-C(50)	1.5340(11)	C(39)-P(2)-C(27)	100.19(3)
C(50)-C(51)	1.5358(11)	C(33)-P(2)-C(27)	103.13(3)
C(51)-C(52)	1.5184(12)	C(39)-P(2)-Re(1)	123.90(2)
C(53)-C(54)	1.5164(11)	C(33)-P(2)-Re(1)	112.81(2)
C(54)-C(55)	1.5170(14)	C(27)-P(2)-Re(1)	114.099(19)
C(55)-C(56)	1.5097(13)	O(7)-Na(1)-O(3)	92.24(2)
		O(7)-Na(1)-O(5)	126.54(3)
C(2)-Re(1)-C(1)	92.03(3)	O(3)-Na(1)-O(5)	86.49(2)

O(7)-Na(1)-O(6)	99.94(3)	O(3)-C(3)-C(4)	119.61(6)
O(3)-Na(1)-O(6)	99.19(2)	O(3)-C(3)-Re(1)	143.20(5)
O(5)-Na(1)-O(6)	133.05(3)	C(4)-C(3)-Re(1)	97.17(4)
O(7)-Na(1)-O(1)#1	80.95(2)	O(4)-C(4)-C(3)	103.69(5)
O(3)-Na(1)-O(1)#1	163.63(3)	C(6)-C(5)-C(12)	113.01(5)
O(5)-Na(1)-O(1)#1	85.71(2)	C(6)-C(5)-B(1)	110.89(5)
O(6)-Na(1)-O(1)#1	96.65(2)	C(12)-C(5)-B(1)	108.74(5)
C(1)-O(1)-Na(1)#2	154.34(5)	C(5)-C(6)-C(7)	115.30(6)
C(3)-O(3)-Na(1)	136.58(5)	C(6)-C(7)-C(8)	115.58(5)
C(4)-O(4)-B(1)	115.25(5)	C(7)-C(8)-C(9)	115.37(5)
C(4)-O(4)-Re(1)	94.98(3)	C(10)-C(9)-C(8)	112.12(5)
B(1)-O(4)-Re(1)	130.01(3)	C(10)-C(9)-B(1)	109.58(5)
C(45)-O(5)-C(48)	106.27(5)	C(8)-C(9)-B(1)	110.31(5)
C(45)-O(5)-Na(1)	124.85(5)	C(11)-C(10)-C(9)	114.91(6)
C(48)-O(5)-Na(1)	121.68(5)	C(10)-C(11)-C(12)	114.81(6)
C(52)-O(6)-C(49)	106.20(6)	C(11)-C(12)-C(5)	114.75(5)
C(52)-O(6)-Na(1)	127.23(5)	C(18)-C(13)-C(14)	118.58(6)
C(49)-O(6)-Na(1)	123.42(5)	C(18)-C(13)-P(1)	120.39(5)
C(53)-O(7)-C(56)	109.87(6)	C(14)-C(13)-P(1)	120.98(5)
C(53)-O(7)-Na(1)	132.02(5)	C(15)-C(14)-C(13)	120.54(7)
C(56)-O(7)-Na(1)	115.61(5)	C(16)-C(15)-C(14)	120.28(8)
O(4)-B(1)-C(5)	107.99(5)	C(15)-C(16)-C(17)	119.66(7)
O(4)-B(1)-C(9)	109.28(5)	C(16)-C(17)-C(18)	120.11(7)
C(5)-B(1)-C(9)	105.00(5)	C(17)-C(18)-C(13)	120.81(7)
O(4)-B(1)-C(26)	108.77(5)	C(24)-C(19)-C(20)	118.61(6)
C(5)-B(1)-C(26)	113.00(5)	C(24)-C(19)-P(1)	119.20(5)
C(9)-B(1)-C(26)	112.64(5)	C(20)-C(19)-P(1)	122.12(5)
O(1)-C(1)-Re(1)	177.26(6)	C(21)-C(20)-C(19)	120.72(7)
O(2)-C(2)-Re(1)	179.19(6)	C(22)-C(21)-C(20)	120.28(7)

C(23)-C(22)-C(21)	119.49(6)	O(5)-C(45)-C(46)	104.39(6)
C(22)-C(23)-C(24)	120.43(7)	C(45)-C(46)-C(47)	103.03(6)
C(23)-C(24)-C(19)	120.44(6)	C(46)-C(47)-C(48)	104.34(6)
C(26)-C(25)-P(1)	111.42(4)	O(5)-C(48)-C(47)	106.45(6)
C(25)-C(26)-B(1)	115.39(5)	O(6)-C(49)-C(50)	106.36(6)
C(32)-C(27)-C(28)	118.38(7)	C(49)-C(50)-C(51)	104.53(6)
C(32)-C(27)-P(2)	123.63(5)	C(52)-C(51)-C(50)	103.12(6)
C(28)-C(27)-P(2)	117.82(6)	O(6)-C(52)-C(51)	104.85(6)
C(29)-C(28)-C(27)	120.70(8)	O(7)-C(53)-C(54)	105.70(7)
C(30)-C(29)-C(28)	120.41(8)	C(53)-C(54)-C(55)	102.21(7)
C(31)-C(30)-C(29)	119.39(7)	C(56)-C(55)-C(54)	102.63(7)
C(30)-C(31)-C(32)	120.35(8)	O(7)-C(56)-C(55)	106.32(8)
C(27)-C(32)-C(31)	120.75(7)		
C(34)-C(33)-C(38)	118.51(6)		
C(34)-C(33)-P(2)	119.48(5)		
C(38)-C(33)-P(2)	121.90(5)		
C(35)-C(34)-C(33)	120.58(7)		
C(34)-C(35)-C(36)	120.43(8)		
C(37)-C(36)-C(35)	119.41(7)		
C(36)-C(37)-C(38)	120.51(7)		
C(37)-C(38)-C(33)	120.56(7)		
C(40)-C(39)-C(44)	119.43(6)		
C(40)-C(39)-P(2)	118.51(5)		
C(44)-C(39)-P(2)	121.73(5)		
C(39)-C(40)-C(41)	120.23(6)		
C(42)-C(41)-C(40)	119.98(8)		
C(43)-C(42)-C(41)	120.00(6)		
C(42)-C(43)-C(44)	120.33(7)		
C(43)-C(44)-C(39)	119.98(7)		

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z

#2 x+1,y,z

Table 5. Anisotropic displacement parameters ($Å^2x\ 10^4$) for $[Na(THF)_3][3\text{-}E_1Ph_1]$ (AJMM48) (CCDC 770346). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Re(1)	61(1)	68(1)	69(1)	-10(1)	-2(1)	-28(1)
P(1)	79(1)	80(1)	79(1)	-15(1)	-2(1)	-32(1)
P(2)	88(1)	81(1)	103(1)	-22(1)	0(1)	-34(1)
Na(1)	117(1)	148(1)	134(1)	27(1)	-28(1)	-70(1)
O(1)	108(2)	229(3)	202(2)	19(2)	-22(2)	-95(2)
O(2)	225(2)	172(2)	114(2)	34(2)	-31(2)	-67(2)
O(3)	97(2)	173(2)	136(2)	6(2)	3(1)	-77(2)
O(4)	76(2)	107(2)	95(2)	5(1)	-10(1)	-45(1)
O(5)	206(2)	239(3)	152(2)	74(2)	-73(2)	-154(2)
O(6)	193(2)	151(2)	237(2)	46(2)	-85(2)	-92(2)
O(7)	213(2)	226(3)	145(2)	-18(2)	-22(2)	-92(2)
B(1)	90(2)	101(2)	88(2)	4(2)	-14(2)	-40(2)
C(1)	98(2)	107(2)	108(2)	-3(2)	-19(2)	-42(2)
C(2)	114(2)	103(2)	102(2)	-11(2)	-5(2)	-42(2)
C(3)	88(2)	101(2)	104(2)	-11(2)	-4(2)	-44(2)
C(4)	90(2)	146(2)	115(2)	15(2)	-19(2)	-62(2)
C(5)	98(2)	121(2)	95(2)	4(2)	-15(2)	-51(2)
C(6)	106(2)	166(3)	129(2)	-30(2)	3(2)	-54(2)
C(7)	156(3)	222(3)	113(2)	-38(2)	-2(2)	-92(2)
C(8)	140(2)	177(3)	113(2)	-4(2)	-33(2)	-79(2)
C(9)	99(2)	131(2)	105(2)	15(2)	-25(2)	-49(2)
C(10)	141(2)	144(3)	144(2)	38(2)	-53(2)	-53(2)
C(11)	173(3)	162(3)	159(2)	57(2)	-51(2)	-95(2)
C(12)	137(2)	151(3)	149(2)	24(2)	-33(2)	-87(2)

C(13)	117(2)	100(2)	95(2)	-17(2)	-21(2)	-39(2)
C(14)	172(3)	169(3)	162(2)	28(2)	-69(2)	-103(2)
C(15)	221(3)	217(3)	243(3)	16(3)	-120(3)	-123(3)
C(16)	227(3)	229(3)	187(3)	-38(2)	-109(2)	-64(3)
C(17)	196(3)	253(4)	109(2)	-14(2)	-43(2)	-48(3)
C(18)	150(2)	186(3)	99(2)	-1(2)	-12(2)	-56(2)
C(19)	99(2)	110(2)	107(2)	-25(2)	7(2)	-37(2)
C(20)	141(2)	121(2)	193(3)	-40(2)	40(2)	-37(2)
C(21)	162(3)	154(3)	247(3)	-68(2)	65(2)	-25(2)
C(22)	145(3)	213(3)	191(3)	-71(2)	57(2)	-55(2)
C(23)	151(3)	196(3)	159(2)	-43(2)	49(2)	-86(2)
C(24)	133(2)	134(2)	132(2)	-30(2)	22(2)	-60(2)
C(25)	127(2)	100(2)	101(2)	-5(2)	-15(2)	-56(2)
C(26)	112(2)	107(2)	109(2)	-8(2)	-20(2)	-23(2)
C(27)	137(2)	101(2)	133(2)	-20(2)	6(2)	-59(2)
C(28)	158(3)	136(3)	354(4)	9(3)	56(3)	-61(2)
C(29)	219(4)	196(4)	394(5)	-16(3)	101(3)	-120(3)
C(30)	294(4)	175(3)	177(3)	-21(2)	41(3)	-153(3)
C(31)	269(4)	126(3)	227(3)	25(2)	-4(3)	-90(3)
C(32)	176(3)	117(3)	223(3)	13(2)	6(2)	-51(2)
C(33)	101(2)	94(2)	169(2)	-32(2)	2(2)	-33(2)
C(34)	123(2)	148(3)	215(3)	-62(2)	-36(2)	-30(2)
C(35)	129(3)	171(3)	334(4)	-78(3)	-66(2)	-25(2)
C(36)	105(2)	146(3)	383(4)	-60(3)	5(3)	-31(2)
C(37)	133(3)	174(3)	275(3)	-29(3)	62(2)	-39(2)
C(38)	130(2)	155(3)	186(3)	-14(2)	28(2)	-35(2)
C(39)	121(2)	123(2)	125(2)	-46(2)	-2(2)	-51(2)
C(40)	171(3)	150(3)	126(2)	-31(2)	-9(2)	-73(2)
C(41)	229(3)	214(3)	129(2)	-34(2)	-24(2)	-94(3)

C(42)	247(3)	250(4)	164(3)	-84(2)	-31(2)	-104(3)
C(43)	264(3)	199(3)	208(3)	-95(3)	-32(3)	-107(3)
C(44)	208(3)	140(3)	177(3)	-51(2)	-24(2)	-80(2)
C(45)	160(3)	164(3)	177(2)	8(2)	-35(2)	-95(2)
C(46)	265(3)	198(3)	149(2)	32(2)	-24(2)	-134(3)
C(47)	294(4)	335(4)	158(3)	85(3)	-87(3)	-188(4)
C(48)	193(3)	232(3)	171(3)	32(2)	-71(2)	-123(3)
C(49)	171(3)	163(3)	180(3)	-18(2)	-49(2)	-57(2)
C(50)	145(3)	134(3)	246(3)	-16(2)	-18(2)	-65(2)
C(51)	274(4)	237(4)	172(3)	37(2)	-52(3)	-132(3)
C(52)	162(3)	190(3)	222(3)	15(2)	-74(2)	-80(2)
C(53)	284(4)	208(3)	177(3)	-25(3)	-51(3)	-2(3)
C(54)	322(4)	209(4)	159(3)	-21(2)	-19(3)	-31(3)
C(55)	405(5)	192(4)	262(4)	-39(3)	-65(3)	-84(4)
C(56)	394(5)	228(4)	256(4)	30(3)	-114(3)	-110(4)

Table 1. Crystal data and structure refinement for 12 (AJMM50) (CCDC 738920).

Empirical formula	$C_{45}H_{48}BO_4P_2Re \bullet ½ (C_6H_5Cl)$
Formula weight	968.06
Crystallization Solvent	Chlorobenzene
Crystal Habit	Block
Crystal size	0.27 x 0.22 x 0.19 mm^3
Crystal color	Yellow

Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 9655 reflections used in lattice determination	2.42 to 53.01°	
Unit cell dimensions	a = 11.4898(4) Å	α= 80.831(2)°
	b = 13.5141(5) Å	β= 84.498(2)°
	c = 15.1385(5) Å	γ = 64.883(2)°
Volume	2100.11(13) $Å^3$	
Z	2	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.531 Mg/m^3	
F(000)	978	
θ range for data collection	1.68 to 53.10°	
Completeness to θ = 53.10°	94.1 %	

Index ranges	$-24 \leq h \leq 25, -23 \leq k \leq 30, -34 \leq l \leq 34$
Data collection scan type	ω scans; 31 settings
Reflections collected	217105
Independent reflections	47162 [R_{int}= 0.0360]
Absorption coefficient	3.045 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7505 and 0.6061

Table 1 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	47162 / 0 / 540
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.413
Final R indices [$I>2\sigma(I)$, 40639 reflections]	R1 = 0.0243, *w*R2 = 0.0396
R indices (all data)	R1 = 0.0350, *w*R2 = 0.0405
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.007
Average shift/error	0.000
Largest diff. peak and hole	3.557 and -2.787 e.Å^{-3}

Special Refinement Details

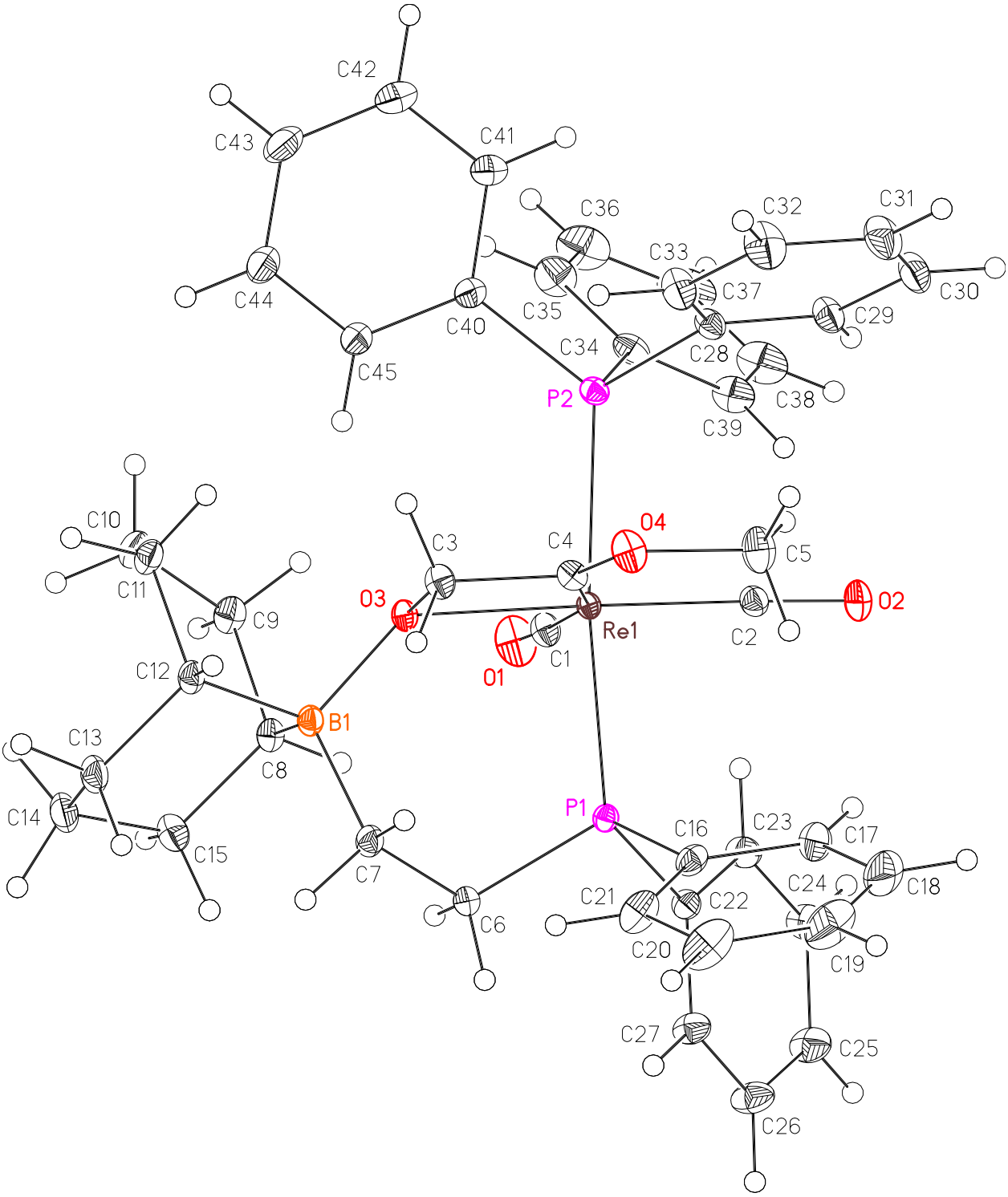
Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

The crystal contains chlorobenzene as a solvent of crystallization and occupies a site near a center of symmetry, occupancy = ½. Additionally, the chlorine position is disordered over two sites in a 4:1 ratio and was modeled as such. The benzene ring was constrained to an ideal hexagon and aside from riding hydrogen atoms no other restraints were applied.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of F^2 >

$2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.


C42
C43
C41
C36
C32
C31
C33
C44
C35
C37
C30
C40
C29
C34
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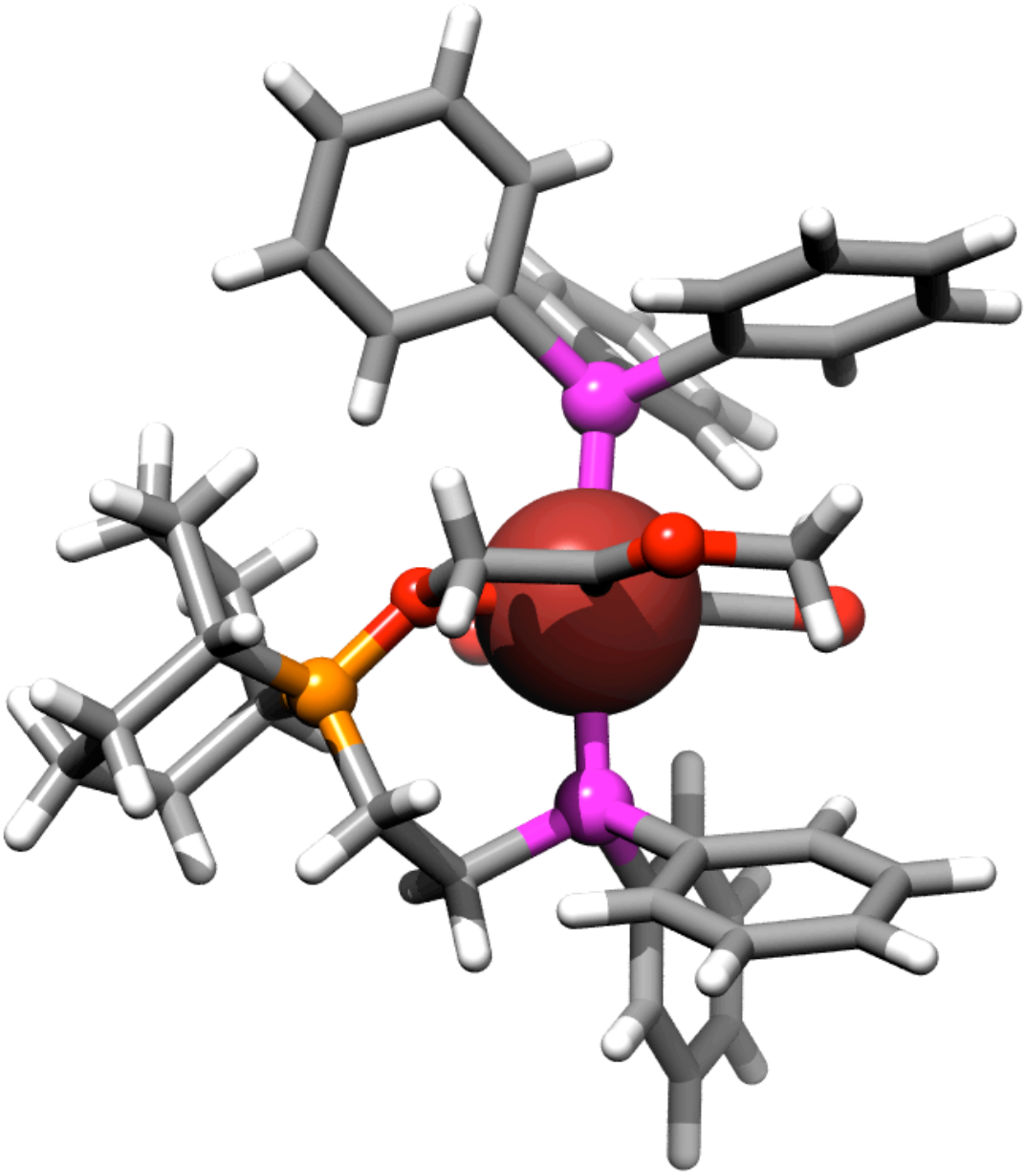
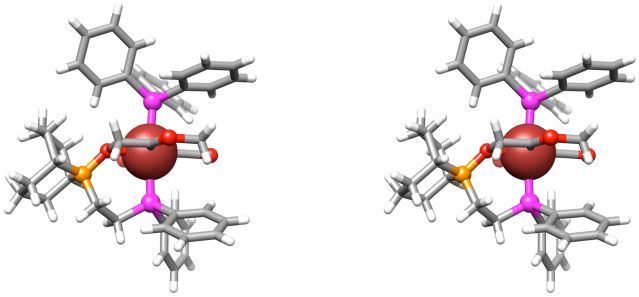
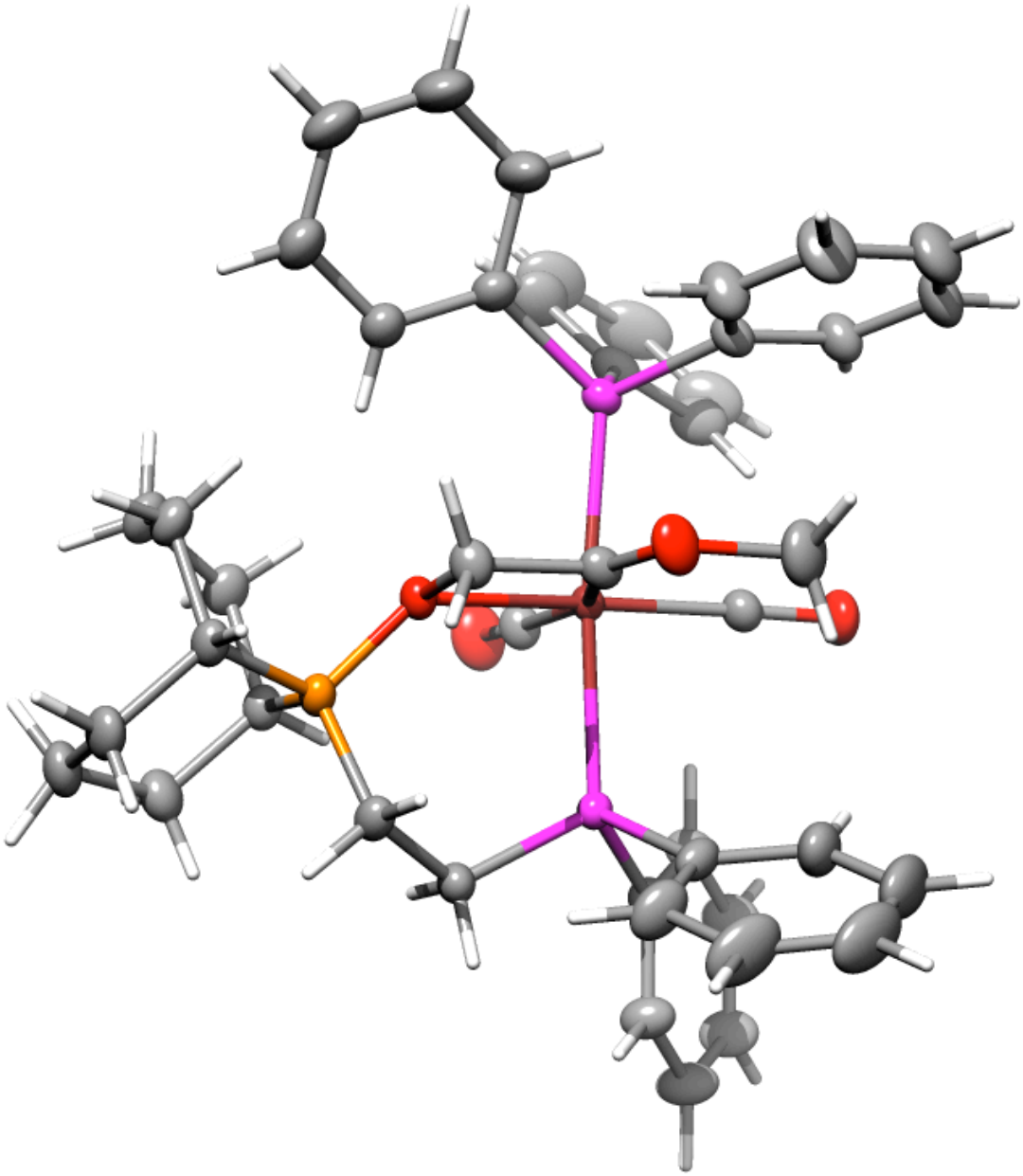
C45
P2
C38
C39
C10
C3
C4
04
C5
C11
03
02
C9
Re1
C2
C1
01
C12
B1
C13
C8
P1
C14
C16
C23
C17
C15
C7
C24
C18
C21
C22
C6
C20
C19
C27
C25
C26







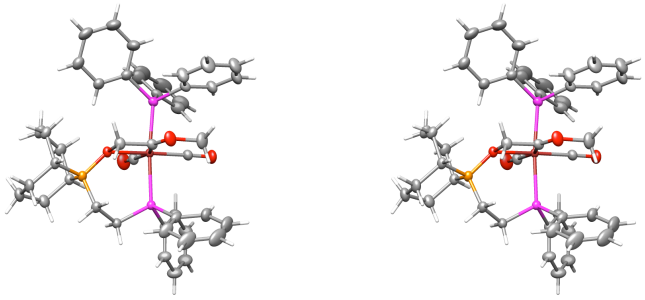


Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 12 (AJMM50) (CCDC 738920). U(eq) is defined at he trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
Re(1)	3818(1)	4048(1)	2615(1)	8(1)	1
P(1)	1838(1)	5510(1)	2043(1)	9(1)	1
P(2)	5815(1)	2700(1)	3303(1)	10(1)	1
O(1)	2332(1)	2840(1)	3843(1)	22(1)	1
O(2)	3809(1)	5574(1)	3901(1)	18(1)	1
O(3)	3967(1)	3220(1)	1424(1)	10(1)	1
O(4)	5521(1)	4971(1)	1244(1)	16(1)	1
B(1)	2861(1)	3221(1)	867(1)	11(1)	1
C(1)	2856(1)	3308(1)	3407(1)	13(1)	1
C(2)	3813(1)	4965(1)	3427(1)	12(1)	1
C(3)	4807(1)	3665(1)	932(1)	13(1)	1
C(4)	4853(1)	4404(1)	1554(1)	11(1)	1
C(5)	5552(1)	5752(1)	1794(1)	20(1)	1
C(6)	1032(1)	5184(1)	1219(1)	12(1)	1
C(7)	1918(1)	4499(1)	507(1)	13(1)	1
C(8)	2129(1)	2560(1)	1504(1)	12(1)	1
C(9)	3102(1)	1418(1)	1905(1)	15(1)	1
C(10)	4032(1)	708(1)	1221(1)	16(1)	1
C(11)	4531(1)	1331(1)	445(1)	14(1)	1
C(12)	3552(1)	2479(1)	63(1)	12(1)	1
C(13)	2529(1)	2420(1)	-491(1)	16(1)	1
C(14)	1607(1)	1997(1)	70(1)	18(1)	1
C(15)	1101(1)	2504(1)	945(1)	17(1)	1
C(16)	1993(1)	6766(1)	1508(1)	13(1)	1

C(17)	2210(1)	7422(1)	2046(1)	21(1)	1
C(18)	2326(1)	8386(1)	1662(1)	28(1)	1
C(19)	2215(1)	8708(1)	746(1)	30(1)	1
C(20)	1984(1)	8073(1)	208(1)	28(1)	1
C(21)	1880(1)	7100(1)	589(1)	19(1)	1
C(22)	533(1)	6112(1)	2854(1)	11(1)	1
C(23)	664(1)	5815(1)	3776(1)	15(1)	1
C(24)	-351(1)	6322(1)	4364(1)	18(1)	1
C(25)	-1518(1)	7117(1)	4036(1)	19(1)	1
C(26)	-1660(1)	7410(1)	3118(1)	19(1)	1
C(27)	-647(1)	6921(1)	2532(1)	16(1)	1
C(28)	6906(1)	3366(1)	3347(1)	13(1)	1
C(29)	6885(1)	3922(1)	4051(1)	15(1)	1
C(30)	7661(1)	4494(1)	4011(1)	20(1)	1
C(31)	8474(1)	4503(1)	3278(1)	22(1)	1
C(32)	8511(1)	3942(1)	2577(1)	24(1)	1
C(33)	7728(1)	3382(1)	2604(1)	19(1)	1
C(34)	5597(1)	2133(1)	4461(1)	14(1)	1
C(35)	6026(1)	995(1)	4709(1)	21(1)	1
C(36)	5828(1)	574(1)	5588(1)	27(1)	1
C(37)	5227(1)	1275(1)	6224(1)	28(1)	1
C(38)	4786(1)	2409(1)	5984(1)	24(1)	1
C(39)	4948(1)	2834(1)	5103(1)	18(1)	1
C(40)	6902(1)	1480(1)	2803(1)	14(1)	1
C(41)	8198(1)	936(1)	3042(1)	24(1)	1
C(42)	9042(1)	60(1)	2612(1)	28(1)	1
C(43)	8622(1)	-298(1)	1945(1)	22(1)	1
C(44)	7334(1)	208(1)	1731(1)	19(1)	1
C(45)	6476(1)	1096(1)	2157(1)	15(1)	1

Cl(1A)	-1382(2)	11699(1)	5630(1)	84(1)	0.403(1)
Cl(1B)	766(3)	11349(3)	4151(3)	42(1)	0.097(1)
C(1A)	-512(2)	10429(1)	5294(1)	41(1)	0.50
C(2A)	-870(1)	9578(2)	5640(1)	44(1)	0.50
C(3A)	-192(2)	8536(1)	5380(1)	45(1)	0.50
C(4A)	843(2)	8345(1)	4772(1)	43(1)	0.50
C(5A)	1200(1)	9195(2)	4426(1)	48(1)	0.50
C(6A)	523(2)	10237(1)	4686(1)	46(1)	0.50

Table 3. Selected bond lengths [Å] and angles [°] for 12 (AJMM50) (CCDC 738920).

Re(1)-C(2)	1.8772(7)	C(2)-Re(1)-C(1)	96.56(3)
Re(1)-C(1)	1.9902(6)	C(2)-Re(1)-C(4)	102.85(3)
Re(1)-C(4)	2.0250(6)	C(1)-Re(1)-C(4)	160.43(3)
Re(1)-O(3)	2.2263(5)	C(2)-Re(1)-O(3)	166.69(2)
Re(1)-P(1)	2.41848(19)	C(1)-Re(1)-O(3)	96.39(2)
Re(1)-P(2)	2.44409(18)	C(4)-Re(1)-O(3)	64.40(2)
		C(2)-Re(1)-P(1)	88.19(2)
		C(1)-Re(1)-P(1)	91.36(2)
		C(4)-Re(1)-P(1)	91.775(18)
		O(3)-Re(1)-P(1)	88.397(13)
		C(2)-Re(1)-P(2)	85.75(2)
		C(1)-Re(1)-P(2)	89.333(19)
		C(4)-Re(1)-P(2)	89.574(18)
		O(3)-Re(1)-P(2)	97.503(13)
		P(1)-Re(1)-P(2)	173.947(6)

Table 4. Bond lengths [Å] and angles [°] for 12 (AJMM50) (CCDC 738920).

Re(1)-C(2)	1.8772(7)	C(11)-C(12)	1.5371(9)
Re(1)-C(1)	1.9902(6)	C(12)-C(13)	1.5438(9)
Re(1)-C(4)	2.0250(6)	C(13)-C(14)	1.5360(11)
Re(1)-O(3)	2.2263(5)	C(14)-C(15)	1.5379(12)
Re(1)-P(1)	2.41848(19)	C(16)-C(21)	1.3936(11)
Re(1)-P(2)	2.44409(18)	C(16)-C(17)	1.4028(11)
P(1)-C(22)	1.8299(7)	C(17)-C(18)	1.3952(11)
P(1)-C(6)	1.8303(6)	C(18)-C(19)	1.3860(17)
P(1)-C(16)	1.8326(6)	C(19)-C(20)	1.3872(16)
P(2)-C(40)	1.8224(8)	C(20)-C(21)	1.3984(10)
P(2)-C(34)	1.8364(7)	C(22)-C(23)	1.3924(10)
P(2)-C(28)	1.8386(6)	C(22)-C(27)	1.4031(9)
O(1)-C(1)	1.1466(8)	C(23)-C(24)	1.3932(11)
O(2)-C(2)	1.1732(9)	C(24)-C(25)	1.3907(10)
O(3)-C(3)	1.4359(8)	C(25)-C(26)	1.3877(11)
O(3)-B(1)	1.5897(8)	C(26)-C(27)	1.3836(11)
O(4)-C(4)	1.3079(7)	C(28)-C(29)	1.3915(11)
O(4)-C(5)	1.4573(10)	C(28)-C(33)	1.4011(10)
B(1)-C(8)	1.6262(9)	C(29)-C(30)	1.3991(10)
B(1)-C(12)	1.6269(11)	C(30)-C(31)	1.3824(13)
B(1)-C(7)	1.6369(9)	C(31)-C(32)	1.3872(14)
C(3)-C(4)	1.4960(10)	C(32)-C(33)	1.3944(10)
C(6)-C(7)	1.5364(11)	C(34)-C(39)	1.3975(12)
C(8)-C(9)	1.5386(9)	C(34)-C(35)	1.3982(11)
C(8)-C(15)	1.5517(9)	C(35)-C(36)	1.3991(12)
C(9)-C(10)	1.5394(12)	C(36)-C(37)	1.3818(17)
C(10)-C(11)	1.5438(10)	C(37)-C(38)	1.3921(14)

C(38)-C(39)	1.3936(11)	O(3)-Re(1)-P(2)	97.503(13)
C(40)-C(45)	1.3904(10)	P(1)-Re(1)-P(2)	173.947(6)
C(40)-C(41)	1.4056(10)	C(22)-P(1)-C(6)	102.40(3)
C(41)-C(42)	1.3836(14)	C(22)-P(1)-C(16)	99.21(3)
C(42)-C(43)	1.3905(14)	C(6)-P(1)-C(16)	104.43(3)
C(43)-C(44)	1.3884(11)	C(22)-P(1)-Re(1)	117.49(2)
C(44)-C(45)	1.3960(12)	C(6)-P(1)-Re(1)	116.58(2)
Cl(1A)-C(1A)	1.7117(19)	C(16)-P(1)-Re(1)	114.39(2)
Cl(1B)-C(6A)	1.708(3)	C(40)-P(2)-C(34)	102.93(3)
C(1A)-C(2A)	1.3900	C(40)-P(2)-C(28)	99.90(3)
C(1A)-C(6A)	1.3900	C(34)-P(2)-C(28)	106.14(3)
C(2A)-C(3A)	1.3900	C(40)-P(2)-Re(1)	122.82(2)
C(3A)-C(4A)	1.3900	C(34)-P(2)-Re(1)	113.95(2)
C(4A)-C(5A)	1.3900	C(28)-P(2)-Re(1)	109.25(2)
C(5A)-C(6A)	1.3900	C(3)-O(3)-B(1)	115.72(5)
		C(3)-O(3)-Re(1)	93.54(4)
C(2)-Re(1)-C(1)	96.56(3)	B(1)-O(3)-Re(1)	129.69(4)
C(2)-Re(1)-C(4)	102.85(3)	C(4)-O(4)-C(5)	117.61(6)
C(1)-Re(1)-C(4)	160.43(3)	O(3)-B(1)-C(8)	108.16(5)
C(2)-Re(1)-O(3)	166.69(2)	O(3)-B(1)-C(12)	107.45(5)
C(1)-Re(1)-O(3)	96.39(2)	C(8)-B(1)-C(12)	105.34(5)
C(4)-Re(1)-O(3)	64.40(2)	O(3)-B(1)-C(7)	108.58(5)
C(2)-Re(1)-P(1)	88.19(2)	C(8)-B(1)-C(7)	113.82(6)
C(1)-Re(1)-P(1)	91.36(2)	C(12)-B(1)-C(7)	113.21(5)
C(4)-Re(1)-P(1)	91.775(18)	O(1)-C(1)-Re(1)	176.85(7)
O(3)-Re(1)-P(1)	88.397(13)	O(2)-C(2)-Re(1)	176.83(6)
C(2)-Re(1)-P(2)	85.75(2)	O(3)-C(3)-C(4)	101.56(5)
C(1)-Re(1)-P(2)	89.333(19)	O(4)-C(4)-C(3)	114.60(6)
C(4)-Re(1)-P(2)	89.574(18)	O(4)-C(4)-Re(1)	145.15(6)

C(3)-C(4)-Re(1)	100.22(4)	C(27)-C(26)-C(25)	120.37(7)
C(7)-C(6)-P(1)	115.63(4)	C(26)-C(27)-C(22)	120.64(7)
C(6)-C(7)-B(1)	115.93(5)	C(29)-C(28)-C(33)	118.69(6)
C(9)-C(8)-C(15)	113.09(6)	C(29)-C(28)-P(2)	123.05(5)
C(9)-C(8)-B(1)	110.64(5)	C(33)-C(28)-P(2)	118.08(5)
C(15)-C(8)-B(1)	108.20(5)	C(28)-C(29)-C(30)	120.47(7)
C(8)-C(9)-C(10)	115.11(6)	C(31)-C(30)-C(29)	120.56(8)
C(9)-C(10)-C(11)	115.74(6)	C(30)-C(31)-C(32)	119.37(7)
C(12)-C(11)-C(10)	116.11(6)	C(31)-C(32)-C(33)	120.54(8)
C(11)-C(12)-C(13)	112.37(6)	C(32)-C(33)-C(28)	120.36(8)
C(11)-C(12)-B(1)	110.18(5)	C(39)-C(34)-C(35)	118.72(7)
C(13)-C(12)-B(1)	110.12(6)	C(39)-C(34)-P(2)	120.48(5)
C(14)-C(13)-C(12)	113.78(6)	C(35)-C(34)-P(2)	120.74(7)
C(13)-C(14)-C(15)	114.32(6)	C(34)-C(35)-C(36)	120.24(9)
C(14)-C(15)-C(8)	115.41(6)	C(37)-C(36)-C(35)	120.48(9)
C(21)-C(16)-C(17)	119.04(6)	C(36)-C(37)-C(38)	119.74(8)
C(21)-C(16)-P(1)	122.19(6)	C(37)-C(38)-C(39)	120.00(10)
C(17)-C(16)-P(1)	118.76(6)	C(38)-C(39)-C(34)	120.73(8)
C(18)-C(17)-C(16)	120.24(9)	C(45)-C(40)-C(41)	119.00(7)
C(19)-C(18)-C(17)	120.15(9)	C(45)-C(40)-P(2)	120.60(5)
C(18)-C(19)-C(20)	120.13(8)	C(41)-C(40)-P(2)	120.36(6)
C(19)-C(20)-C(21)	119.99(9)	C(42)-C(41)-C(40)	120.19(8)
C(16)-C(21)-C(20)	120.44(8)	C(41)-C(42)-C(43)	120.62(7)
C(23)-C(22)-C(27)	118.65(7)	C(44)-C(43)-C(42)	119.48(8)
C(23)-C(22)-P(1)	122.98(5)	C(43)-C(44)-C(45)	120.23(8)
C(27)-C(22)-P(1)	118.36(5)	C(40)-C(45)-C(44)	120.40(6)
C(22)-C(23)-C(24)	120.58(6)	C(2A)-C(1A)-C(6A)	120.0
C(25)-C(24)-C(23)	120.16(7)	C(2A)-C(1A)-Cl(1A)	118.27(12)
C(26)-C(25)-C(24)	119.59(7)	C(6A)-C(1A)-Cl(1A)	121.73(12)

C(1A)-C(2A)-C(3A)	120.0
C(4A)-C(3A)-C(2A)	120.0
C(5A)-C(4A)-C(3A)	120.0
C(4A)-C(5A)-C(6A)	120.0
C(5A)-C(6A)-C(1A)	120.0
C(5A)-C(6A)-Cl(1B)	121.29(19)
C(1A)-C(6A)-Cl(1B)	117.93(18)

Table 5. Anisotropic displacement parameters ($Å^2 x 10^4$) for 12 (AJMM50) (CCDC 738920). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Re(1)	90(1)	90(1)	67(1)	-14(1)	0(1)	-42(1)
P(1)	98(1)	89(1)	83(1)	-14(1)	2(1)	-40(1)
P(2)	100(1)	119(1)	89(1)	-11(1)	-8(1)	-45(1)
O(1)	284(3)	288(3)	153(2)	-20(2)	55(2)	-200(3)
O(2)	219(2)	191(2)	162(2)	-85(2)	-12(2)	-86(2)
O(3)	123(2)	116(2)	83(2)	-23(1)	3(1)	-59(1)
O(4)	205(2)	203(2)	127(2)	-9(2)	23(2)	-145(2)
B(1)	132(2)	101(2)	93(2)	-19(2)	-11(2)	-48(2)
C(1)	145(2)	155(3)	95(2)	-26(2)	9(2)	-75(2)
C(2)	126(2)	136(2)	109(2)	-25(2)	-8(2)	-56(2)
C(3)	149(2)	161(3)	91(2)	-27(2)	17(2)	-79(2)
C(4)	118(2)	124(2)	99(2)	1(2)	-4(2)	-61(2)
C(5)	264(3)	200(3)	192(3)	-31(3)	19(3)	-164(3)
C(6)	120(2)	118(2)	123(2)	-34(2)	-16(2)	-42(2)
C(7)	160(2)	113(2)	103(2)	-22(2)	-21(2)	-42(2)
C(8)	147(2)	125(2)	112(2)	-29(2)	3(2)	-63(2)
C(9)	195(3)	128(3)	126(3)	-8(2)	5(2)	-73(2)
C(10)	209(3)	105(2)	159(3)	-21(2)	-1(2)	-54(2)
C(11)	175(2)	116(2)	129(3)	-40(2)	8(2)	-45(2)
C(12)	161(2)	117(2)	95(2)	-26(2)	-6(2)	-58(2)
C(13)	213(3)	164(3)	118(2)	-49(2)	-25(2)	-76(2)
C(14)	218(3)	178(3)	178(3)	-52(2)	-34(3)	-105(2)
C(15)	174(3)	193(3)	165(3)	-40(2)	-8(2)	-103(2)
C(16)	123(2)	96(2)	171(3)	-16(2)	16(2)	-47(2)
C(17)	224(3)	135(3)	283(4)	-35(3)	-48(3)	-87(2)
C(18)	269(4)	148(3)	470(6)	-54(3)	-26(4)	-122(3)
C(19)	297(4)	145(3)	462(6)	5(3)	73(4)	-122(3)

C(20)	340(4)	166(3)	280(4)	34(3)	96(3)	-108(3)
C(21)	244(3)	131(3)	172(3)	2(2)	54(3)	-81(2)
C(22)	111(2)	126(2)	105(2)	-25(2)	9(2)	-48(2)
C(23)	125(2)	193(3)	106(2)	-29(2)	0(2)	-45(2)
C(24)	156(3)	246(3)	113(3)	-39(2)	18(2)	-51(2)
C(25)	146(2)	231(3)	144(3)	-46(2)	37(2)	-36(2)
C(26)	136(2)	209(3)	154(3)	-21(2)	18(2)	-10(2)
C(27)	141(2)	166(3)	119(3)	-12(2)	7(2)	-25(2)
C(28)	108(2)	167(3)	114(2)	-31(2)	2(2)	-64(2)
C(29)	149(2)	211(3)	132(3)	-52(2)	3(2)	-94(2)
C(30)	190(3)	252(3)	199(3)	-78(3)	-12(3)	-128(3)
C(31)	197(3)	292(4)	260(4)	-71(3)	12(3)	-166(3)
C(32)	204(3)	347(4)	242(4)	-92(3)	85(3)	-185(3)
C(33)	174(3)	270(4)	162(3)	-83(3)	50(2)	-132(3)
C(34)	139(2)	186(3)	112(2)	19(2)	-31(2)	-82(2)
C(35)	252(3)	194(3)	181(3)	44(3)	-45(3)	-111(3)
C(36)	306(4)	270(4)	233(4)	111(3)	-58(3)	-146(3)
C(37)	259(4)	389(5)	173(3)	110(3)	-28(3)	-160(4)
C(38)	218(3)	359(5)	126(3)	17(3)	16(3)	-122(3)
C(39)	170(3)	235(3)	123(3)	5(2)	7(2)	-81(2)
C(40)	138(2)	124(2)	149(3)	-23(2)	-23(2)	-30(2)
C(41)	157(3)	221(3)	296(4)	-104(3)	-73(3)	3(2)
C(42)	178(3)	220(4)	356(5)	-102(3)	-67(3)	23(3)
C(43)	204(3)	136(3)	262(4)	-53(3)	-2(3)	-4(2)
C(44)	211(3)	138(3)	200(3)	-47(2)	-20(3)	-39(2)
C(45)	157(2)	127(2)	156(3)	-27(2)	-21(2)	-42(2)

Cl(1A)	1139(12)	290(4)	843(11)	-101(5)	-692(10)	86(5)
Cl(1B)	424(16)	302(14)	540(20)	41(13)	-96(14)	-181(12)
C(1A)	411(12)	388(13)	429(15)	20(10)	-238(12)	-141(10)
C(2A)	332(11)	581(17)	453(16)	47(13)	-211(11)	-230(11)
C(3A)	509(15)	387(13)	525(18)	17(12)	-287(15)	-215(12)

C(4A)	499(16)	390(14)	387(15)	-71(12)	-215(13)	-121(12)
C(5A)	395(12)	628(19)	415(15)	-55(13)	-174(12)	-187(13)
C(6A)	555(17)	559(17)	402(15)	87(13)	-218(13)	-370(15)

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